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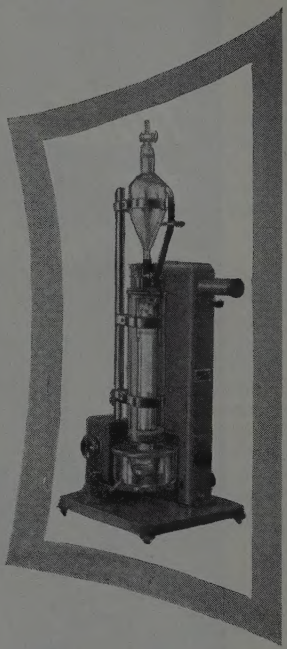

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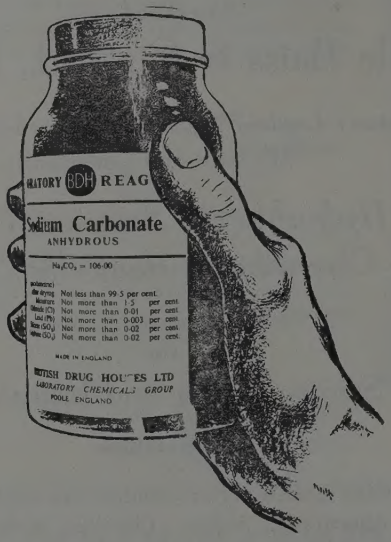

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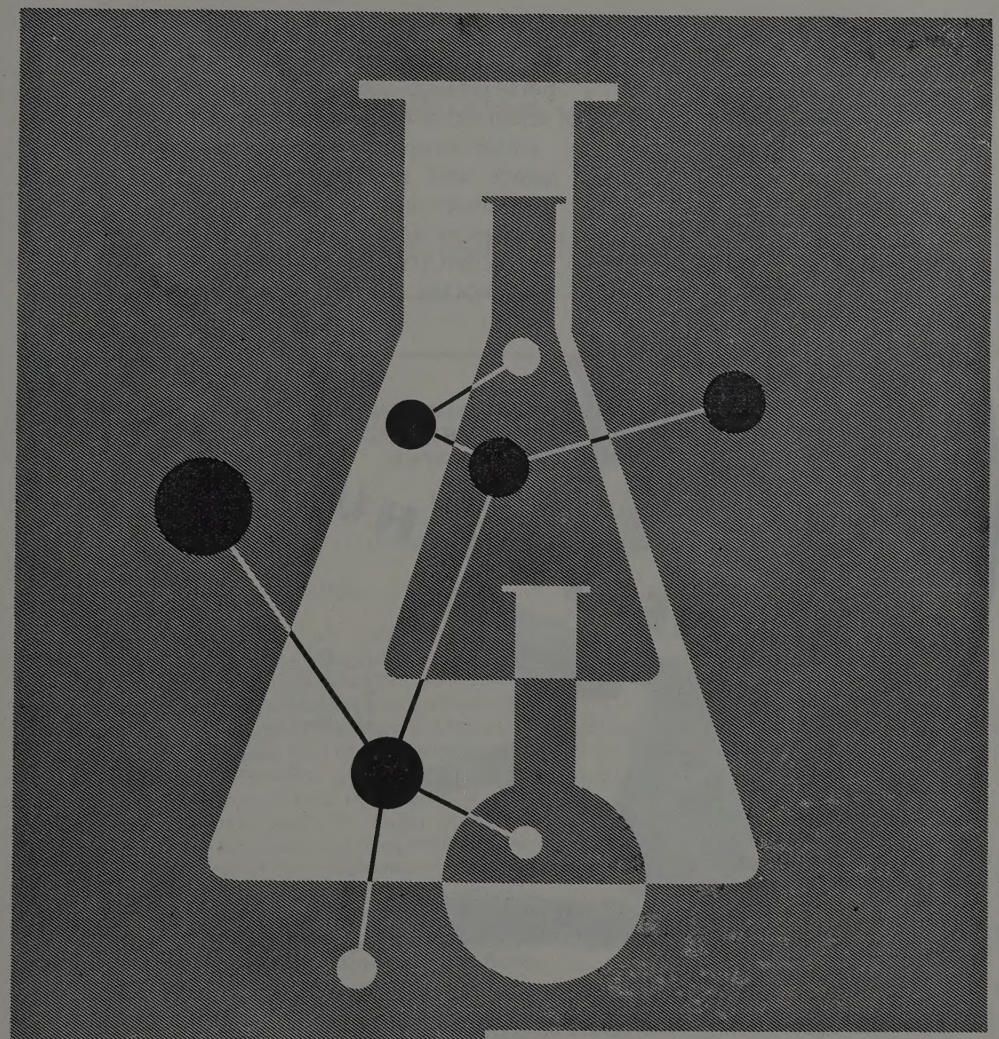

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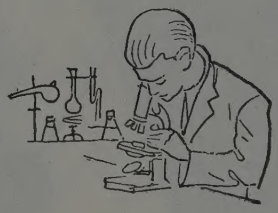

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STUDIES ON THE DISTRIBUTION, GROWTH, AND CELLULOLYTIC ACTIVITY OF FUNGUS ORGANISMS CAUSING DETERIORATION OF RAW AND FINISHED PRODUCTS

Rabia Khanum* and Q. A. Ahmed†

Department of Botany, University of Dacca, Dacca, East Pakistan

Introduction

Fungal deterioration of all kinds of raw and finished goods is a severe problem in East Pakistan, because the climatic conditions are such as to furnish nearly optimum temperature and humidity during the six rainy months from May to October.[1] This fungal deterioration is of especial importance in the storage of cotton yarn and jute fibres, and therefore it was considered of importance to undertake a systematic study of fungal deterioration with reference to: (1) the most frequently occurring fungus organisms in mildewed materials, (2) the optimum conditions for their growth, and (3) their cellulolytic activity with reference to cotton and jute fibres. The present communication describes the results obtained in these three directions.

Distribution of Fungus Organisms Isolated from Deteriorated Materials

A systematic isolation of fungus organisms from various mildewed substrata such as cotton fabrics, jute fibres, leather articles, paper, rexin coverings, camera lenses and other industrial finished products was carried out. Altogether a total of 24 organisms were isolated from the above sources.

The medium used for isolation was Waksman's glucose peptone medium (glucose 10 g., peptone, 5 g.; potassium dihydrogen phosphate 1.0 g.; magnesium sulphate 0.5 g.; agar, 20 g.; water 1000 ml.; adjusted to *p*H 3.8-4).

To each sterilised petri dish about 20 ml. of sterilised medium was added. After the medium had solidified the isolation was made in several ways as follows :

(i) Spores were dusted or discharged naturally over the medium.
(ii) Spores were transferred by touching the head of the organisms with a sterile needle.
(iii) Spores were discharged over the medium by scraping the substrata, such as leather goods, rexin coverings etc., by means of a sterile scalpel.
(iv) In case of cotton threads, jute fibres etc., the infected portions were cut into small pieces, transferred to culture dishes by means of sterile forceps and placed on the medium.

The culture dishes were incubated at 30°C. for 3-5 days before isolation could be made. In many cases a second or third isolation had to be made for freeing from bacterial and fungal contaminations. Single hyphal and monosporic cultures were made finally for obtaining pure culture.

For the identification of *Penicillium* and

*At present Lecturer in Botany, Dacca College, Dacca.
†At present Plant Pathologist, Jute Research Institute, Dacca.

Aspergillus species Czapeck's medium (sodium nitrate, 2 g.; potassium hydrogen phosphate, 1.0 g.; potassium chloride 0.5 g.; magnesium sulphate 0.5 g.; ferrous sulphate 0.01 g.; sucrose, 30 g.; agar, 20 g.; water 1000 ml.) was used. Raper and Thom[2] used this medium for specific identification. For other fungi potato dextrose agar medium (peeled potato, 200 g.; glucose, 20 g.; agar, 20 g.; water, 1000 ml.) was used and identification was made from Gilman's[3] "Soil Fungi" and from Smith's[4] "Introduction to Industrial Mycology."

The organisms isolated from different substrata have been listed in Table 1.

It will be seen from the above table that *Penicillium* and *Aspergillus* appeared most widely in most of the mildewed articles and they were represented by 10 and 7 species respectively. *Memnoniella echinata* has been found to cause damage to many items made up of cotton fabrics when exposed to the weather condition in humid tropical areas.[4] Among other organisms *Curvularia lunata* and *Fusarium conglutinans* from Vita glucose tablets, *Paecilomyces* sp. from camera lens, *Chaetomium globosum*, *Trichoderma lignorum* and *Cunninghamella* sp. from jute sackings may be mentioned.

Spore Germination Tests in Relation to Controlled Humidity

The next step in the present study was to determine the influence of relative humidity upon the germination and the elongation of germ tubes of the fungi *Memnoniella echinata*, *Penicillium terlikowskii*, *P. funiculosum* and *Chaetomium globosum* isolated from deteriorated cotton fabrics and jute sackings in the previous experiment. For the case of *Aspergillus niger*, Bonner[5] could find the relative humidity requirement for the germination to be as low as 70%.

A simple method of conducting such test was devised following Clayton's[6] work by suspending cover glasses with spores of the test organisms over different solutions supposed to produce theoretically definite humidity. Salt of oxalic acid of analytical reagent grade, analyzed sucrose, and redistilled water were used in the preparation of the required solutions.

The humidity chambers were set up by a series of air-tight wide-mouthed bottles (250 ml. capacity) having their lids and upper region of the neck portion grounded. The chambers were thoroughly cleaned and washed with redistilled water.

The experiment was carried out with 100, 99.85, 99.04, 99.03, and 96.0% relative humidities. These were respectively made out of redistilled water, 0.10, 0.50, 1.0 molar solutions of sucrose and saturated solutions of oxalic acid.[6]

TABLE 1.—LIST OF FUNGI ISOLATED FROM THE RESPECTIVE SUBSTRATA.

Fungi	Substrata
Aspergillus flavus ..	leather
A. fumigatus	leather, Vita glucose
A. luchuensis	jute, cotton
A. niger	cotton
A. ruber	leather
A. sydowi	leather, condensed milk
A. terreus	cotton
Chaetomium globosum ..	jute
Curvularia lunata ..	Vita glucose
Cunninghamella sp. ..	jute
Fusarium conglutinans ..	Vita glucose
Memnoniella echinata ..	cotton
Paecilomyces sp. ..	lens
Penicillium adametzi ..	silk
P. canescens	paper
P. charlesii	leather
P. citrinum	paper, condensed milk
P. funiculosum ..	jute
P. phoenicium	tobacco
P. restrictum	rexin, Vita glucose
P. terlikowskii ..	cotton, leather, wool
Penicillium sp. ..	cotton
Penicillium sp. ..	paper
Trichoderma lignorum ..	jute

To each of the humidity chambers for 99.85, 99.04, and 98.03 percentages of relative humidity, was added 46 ml. of the respective molar solutions of sucrose. The chambers were then autoclaved at 100°C. for 10 minutes to inactivate enzyme possibly present in sucrose. Later, 10 mg. of potassium dichromate was dissolved in 4 ml. of water and was added to each of the chambers after they had cooled. Potassium dichromate was added to prevent the growth of any organisms in these sucrose solutions. To the remaining two sets of humidity chambers, one received 50 ml. of redistilled water for giving 100% humidity, the other one received 50 ml. of saturated oxalic acid solution and thus used for the purpose of humidity chamber giving 96.0% relative humidity.

Cover glasses used as spore-carriers were thoroughly cleaned in acid and rinsed several times in distilled water and kept for 24 hours in redistilled water and dried with clean cloth. Non-nutritive spore carriers were used because the presence of extraneous material would effect the relative humidity surrounding the spores.[6]

Spores were brushed over the cover glass. Each spore carrier was then attached to one end of a glass rod with paraffin. The paraffin was heated before its use to get rid of any volatile materials. The lower end of the glass rod bearing the spore carrier was embedded on a glass ring which was attached to the glass lid of the humidity chamber with paraffin (Fig. 1). Three such spore-carriers were embedded in each humidity chamber. The chambers were shaken gently at regular intervals of time taking care that no splashing of the solution within them occurred. This was done to minimize stratification of atmosphere or of the solution within the chamber.

Fig.I.— Spore carrier and humidity chamber.

At the end of each test spores were stained with cotton blue glycerine and observed under microscope for making counts. The germinated spores with their germ tubes this way stained blue and helped easy counting and observation. Spores mounted in this way also could be kept for long time for later observation.

Rectangular cover glasses were used in this experiment for carrying spores of the organisms to be tested. Spores were brushed at one end of the cover glass and this end remained suspended towards the solution inside the chamber and examined after 24 and 48 hours incubation at 30-31°C. Usually ten counts were taken from one end of the cover glass to the other, pushing it horizontally and from ten different microscopical fields. For finding out percentage of germination altogether about 1000 spores were counted for each of the organisms, *M. echinata*, *P. terlikowskii* and *P. funiculosum* while with *Ch. globosum*, a little over 500 ascospores were observed. The length of the germ tubes were measured by means of ocular micrometer and the mean result of 10 measurements are noted in Table 2.

Data presented in Table 2 showed that with all the four organisms tested the higher the relative humidity the greater was the percentage of germination of the spores. The mean percentages of germination of spores of the four test organisms at a relative humidity of 100% after 24 hours were between 70-80% and after 48 hours approximately 10% more spores germinated. At relative humidity of 99.85, 99.04 and 98.03%, the germination rates were progressively lower than those obtained at 100%. The mean germination at a relative humidity of 99.85% after 24 hours was 26-31% and after 48 hours 30-36%. Similarly, at 99.04% the mean germination of spores with the four organisms ranged between 20-25% after 24 hours and 25-30% after 48 hours; at 98.03% the figures were 12-16% after 24 hours and 15-17% after 48 hours, whereas germination was zero to very few at 96%.

As noted above the length of the germ tubes were also found to be strongly dependent upon the percentage of relative humidity, an increase from 98% to 100% producing a two to four fold increase in length of the germ tubes.

Assay of Cellulolytic Activity of the important Fungi attacking Cotton Yarns and Jute Fibres

Three species of fungi, *Memnoniella echinata*, *Penicillium terlikowskii* and *Aspergillus niger*

TABLE 2.—GERMINATION OF SPORES AND LENGTH OF GERM TUBES OF FOUR FUNGI AT DIFFERENT RELATIVE HUMIDITY AFTER 24 AND 48 HOURS EXPOSURES.

Organism	Mean germination of spores at relative humidity							
	100%		99.85%		99.04%		98.03%	
	Exposure		Exposure		Exposure		Exposure	
	24 hrs.	48 hrs.	24 hrs.	48 hrs.	24 hrs.	48 hrs.	24 hrs.	48 hrs.
Memnoniella echinata ..	70	88	30	33	24	25	14	16
Penicillium terlikowskii ..	73	87	31	34	25	26	15	16
P. funiculosum	80	90	30	36	23	30	16	17
Chaetomium globosum ..	70	83	26	30	20	27	12	15
	Mean length (in μ) of the germ tubes							
M. echinata	50	78	30	58	26	46	19	21
P. terlikowskii	50	74	27	54	22	47	18	25
P. funiculosum	46	63	32	46	23	34	17	27
Ch. globosum	47	68	39	60	32	51	24	26

isolated from cotton fabrics and two species, *Chaetomium globosum* and *Penicillium funiculosum* from jute sackings were used in this experiment. All determinations on the rate of cellulose decomposition were made with cotton threads and jute fibres, which were cut into a number of equal pieces for the work. About 30 pieces of the threads and fibres were placed on one microscope slide and tied at both their ends. Two such slides were placed in a single pair of petri dishes equipped with two Whatman No. 4 filter papers. Four dishes thus equipped were autoclaved for 15 minutes at 15 lbs. pressure. After cooling 3 ml. sterilised water was added to each dish. Spores were dusted over the sterilised threads and fibres by the help of camel hair brushes, also sterilised previously by autoclaving. After inoculation the plates were kept in a saturated moist chamber. This was made by filling the lower part of a large sized glass dessicator with redistilled water and placing the dishes on the wire-netting which rested over the false bottom.

After incubation at 30–31°C. for the requisite number of days the thread and fibres were removed. Harvesting was accomplished by transferring them to 70% ethanol for several minutes and then washing with distilled water. The excess water was drained and the threads and fibres laid on blotting paper to dry. The dried material was conditioned at 55% relative humidity for 24 hours before the breaking strength was measured.

The breaking strength of the fibres was determined with an apparatus as shown in Fig. 2. This consists of an ordinary balance in which the left pan has been replaced by two clips A and B. A is suspended from the left beam while B is attached to the balance pillar and can be moved up and down by rack and pinion arrangement. A and B lie in the same vertical line.

The fibres were rarely uniform in the true sense of the term as observed under a microscope ; the diameter is never the same throughout. The breaking weight being essentially dependent on the cross sectional area of the fibre, some pieces of cotton yarns and jute fibres at random were examined under a microscope at different parts of their entire length and mean diameter was determined. These mean diameters of different

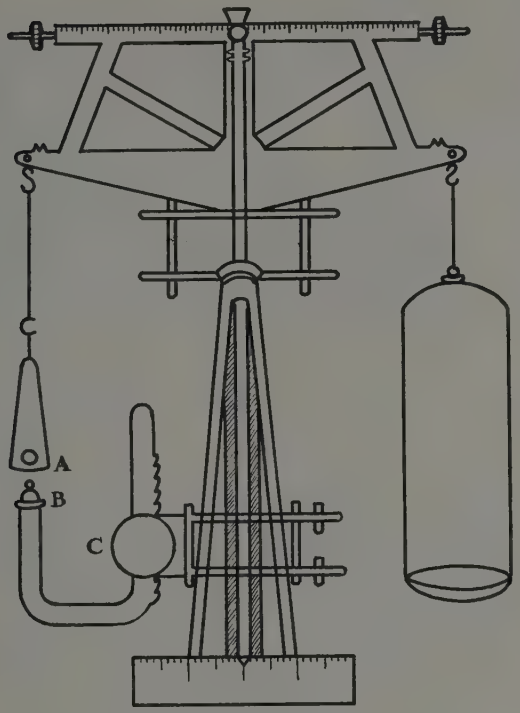

Fig.2.— Showing the parts of the apparatus for determination of breaking strength of fibres.

pieces of cotton yarns and jute fibres though somewhat varied but for the present purpose were considered to be uniform.

After carefully clamping a single fibre at both ends A and B, C was slowly turned to stress the fibre properly so that on releasing the pan the pointer remained at the zero position. The tightening of the fibres by the clamp A and B required the greatest skill ; if it be too tight at either end the fibres break evidently with a lesser weight. When this took place the reading was discarded. The weights were very slowly and gradually increased, for it had been found that a fibre not breaking with a greater weight broke with a smaller one when the latter was placed at once. It was also noticed that at a certain weight the fibre did not break as soon as the beam was raised but only after a few seconds.

The yarn used for the experiments on cotton was of 22 count.* One of the four dishes containing samples, mounted and sterilized as described above, was kept as control and the other three were respectively inoculated with the spores of the test organisms, *M. echinata*, *P. terlikowskii* and *A. niger*, by brushing over the threads. After inoculation the dishes were kept in the moist chamber. Assay of the breaking strength was made after one, two, three, four, and six-weeks' growth of the organisms by taking out each time from each dish about 10 to 12 pieces of cotton yarns, washing, conditioning and then measuring the strength as described above. Fig. 3 shows the mode of growth of *M. echinata* on fibres of cotton yarns.

* By courtesy of No. I Dhakeshwari Cotton Mills, Narayanganj, Dacca.

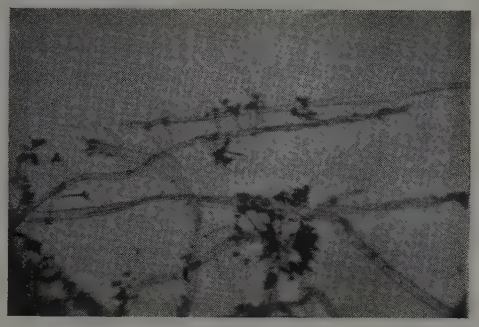

Fig.3.— *Memnoniella echinata* on cotton fibres showingconidiophores and conidia.

With jute fibres similar steps as above were followed. But here the organisms used were *Chaetomium globosum* and *Penicillium funiculosum* and the measurements of the breaking strength started from second week. Figure 4 shows a single perithecium of *Ch. globosum* growing on jute fibres.

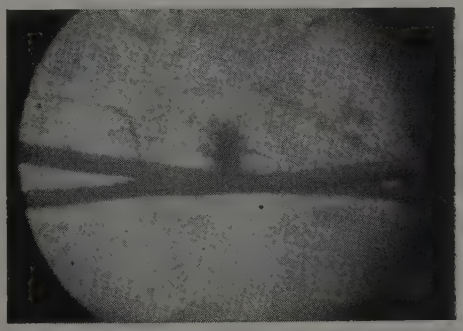

Fig.4.— *Chaetomium globosum* on jute fibres showing a single perithecium

TABLE 3.—COMPARATIVE CELLULOLYTIC ACTIVITY OF THREE SPECIES OF FUNGI AFTER GROWING THEM ON COTTON FIBRES FOR DIFFERENT LENGTHS OF TIME (IN WEEKS).

Week No.	Mean breaking weight of 10 measurements in g.			
	Control	*M. echinata*	*P. terlikowskii*	*A. niger*
First	290.8	230.4	238.5	265.6
Second	282.5	124.0	189.3	217.5
Third	276.8	102.2	178.1	189.2
Fourth	271.0	93.4	131.6	159.8
Sixth	261.8	51.0	100.2	128.7

The mean of the results noted by measuring the breaking strengths of 10 fibres of each kind (cotton and jute) per week per treatment was tabulated in Tables 3 and 4.

Data presented in Table 3 showed the relative destructive abilities of the three test organisms. Within six weeks *M. echinata* reduced the strength of the yarns to one fifth of their original strength and the other two organisms could reduce the strength a little over half with reference to the yarns present in control dishes.

Table 4 showed the relative degradations of jute fibres from week to week with *Chaetomium*

TABLE 4.—COMPARATIVE CELLULOLYTIC ACTIVITY OF TWO SPECIES OF FUNGI ON JUTE FIBRES AT DIFFERENT INTERVALS OF TIME.

Week No.	Mean breaking weight of 10 measurements in g.		
	Control	*Ch. globosum*	*P. funiculosum*
Second	42.2	22.7	34.7
Third	41.1	21.3	29.8
Fourth	40.2	11.9	23.4
Sixth	37.5	7.6	15.1

and *Penicilium* inoculated sets. In the control sets the breaking weights after second week and sixth week were 42.2 and 37.5 g., respectively. During the same corresponding times with *Chaetomium* the weights needed to break the yarns were 22.7 and 7.6 g. With *Penicillium* these breaking weights were respectively 34.7 and 15.1 g.

Conclusions

In this experiment with *Memnoniella echinata* the percentage of loss in breaking strength at 7, 14, 21, 28, and 42 days harvest was approximately 16, 55, 63, 66 and 78, respectively. The breaking strength values for the corresponding harvests were 230.4, 124.0, 102.2, 93.4 and 51.0 g., respectively. The values of the average of controls has been used in all calulations. A small loss of breaking strength was found for the controls during the whole period of the work (Fig. 5), and this may be attributed to stray bacterial contamination occuring when the moist chambers were opened every week for removal of test samples.

The percentage of loss in breaking strength of the cotton yarns with *Penicillium terlikowskii* after 7, 14, 21, 28, and 42 days harvest was approximately 14, 31, 35, 52 and 60, respectively. The breaking strength for corresponding harvests were 238.5, 189.3, 178.1, 131.6 and 100.2 g., respectively. The loss of breaking strength was much less when compared to *Memnoniella echinata*.

With *Aspergillus niger* treated cotton yarns the percentage of loss in breaking strength at the above intervals of time was 4, 21, 32, 42 and

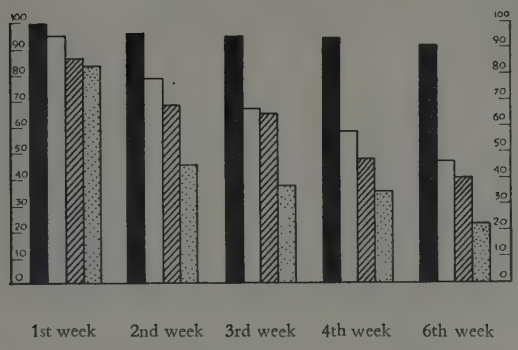

Fig.5.— Percentage of strength of variously treated cotton yarns after five successive periods.

Control yarns.

Yarns on which *Aspergillus niger* had been grown.

Yarns on which *Memnoniella echinata* had been grown.

Yarns on which *Penicillium terlikowskii* had been grown.

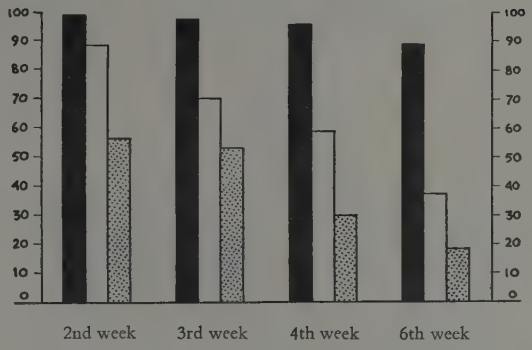

Fig.6.— Percentage of strength of variously treated jute fibres after four successive periods.

Control fibres.

Fibres on which *Penicillium funiculosum* had been grown.

Fibres on which *Chaetomium globosum* had been grown.

53, respectively. Their breaking strengths were respectively 265.6, 217.5, 189.2, 159.8 and 128.7 g.

Among the three fungi tested on cotton yarns *M. echinata* was found to cause greater loss in the breaking strength of the yarns than the other two.

The jute fibres when treated with *Chaetomium globosum* and *Penicillium funiculosum* the percentage of loss in breaking strength with *Chaetomium* was far greater than the *Penicillium*. The percentage of loss in breaking strength after 14, 21, 28 and 42 days harvest was 43, 47, 70 and 81, resepectively, with the *Chaetomium*. In the corresponding intervals of time with *P. funiculosum* the percentage of loss in breaking strength was 11, 30, 41 and 62, respectively (Fig 6).

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AUTOXIDATION REACTIONS IN THE PRESENCE OF LIGHT-SENSITIZED CHLOROPHYLL

NURUL ABSAR KHAN

East Regional Laboratories, Pakistan Council of Scientific and Industrial Research, Tejgaon, Dacca

Introduction

The oxidation of substances under the influence of visible light in the presence of fluorescent pigments, especially chlorophyll, has several interesting aspects : first, the problem of photodynamic action and assimilation of carbon dioxide in the green plant ; second, the chemical and physico-chemical problem of autoxidation and chemical reaction mechanism in general ; third, the industrial utilization of the unlimited supply of solar energy through this energy-trapping natural substance, chlorophyll. The study of oxidation of fatty acid esters (the components of lipids found in all plant cells) by means of photosensitized chlorophyll was therefore taken up specially as it may help elucidating some phases of oxidation of the fatty substances, and throw light on the parameters of the general problem of oxidative metabolism.

From the work of Meyer,[1] Robinowitch[2] and Wassink,[3] the reaction of chlorophyll and oxygen may be summarized as follows :

$$(Chl)^* + A(O_2) \longrightarrow (Chl) + (AO_2)E$$

A being a compound with loose complex $A(O_2)$

$(AO_2)^E = A + O_2 + E$, dependent on temperature and *p*H

$O_2 + Chl^* \longrightarrow O_2^E$, activation of oxygen

Later findings show that

$(Chl) + O_2 \longrightarrow (Chl)O_2$, a dissociable complex.

Chl^* → fluorescence
Chl^* → heat
Chl^* → A_o (absorbing substrate)

Furthermore, chlorophyll can act both as an oxidizing agent and a reducing agent, thus

$$Chl^* + Ox \longrightarrow OChl + rOx$$

$$Chl^* + Red \longrightarrow rChl + O\ Red$$

$$OChl + rChl \longrightarrow 2\ Chl$$

This easily follows from the theory of Weiss[4] who has propounded that an electronically excited molecule has an increased tendency for giving away an electron, as well as a capacity for acquiring an electron to replace the one which was removed from its normal level. Ghosh et al.,[5] found that chlorophyll initiates oxidation-reduction even in the absence of oxygen :

$$Chl^* + MeR \longrightarrow (Chl^*MeR)$$

(methyl red)

$$(Chl^*\ MeR) + Ph \longrightarrow Chl + Leuco\ MeR + oxidized\ Ph.$$

(phenyl hydrazine)

Livingstone et al.[6] confirmed these results and indicated that activated chlorophyll may form complexes with substances other than oxygen, while Franck[7] proposed a two-step process,[8] involving free radicals in the case of photo-chlorophyll oxidation, which concept is supported by the evidence in a recent investigation by Uri.[9]

In order to get a better insight into this mechanism, the stability of chlorophyll in heptane solution has been studied : (a) alone, (b) mixed with a substrate without agitation and (c) mixed with a substrate agitated by oxygen gas both in the presence and in the absence of light. A mixture of methyl oleate and linoleate (6 : 5) has been used to study some effects of temperature and solvent on chlorophyll-sensitized photo-oxidation.

A plausible mechanism involving both complex formation and oxidation reduction has been suggested for the photo-oxidation of methyl oleate and linoleate in the presence of chlorophyll. The results are substantiated by oxidation of simpler organic substances of requisite structure under similar conditions.

Experimental

Materials.—The chlorophyll was extracted from spinach (palang) leaves by means of acetone (200-250 ml./150 g. midrib-free leaves) in a waring blender containing a small amount of magnesium carbonate. Acetone solution, 500 ml., was three times diluted with water and extracted with purified petroleum ether (b.p. 30-60°C.). After

washing the petroleum ether solution with water, it was shaken with several portions of 80% methanol saturated with petroleum ether and containing 0.01 g. oxalic acid to prevent allomerization. The petroleum ether solution, freed of methanol, was dried with anhydrous sodium sulphate. Sufficient dried sugar, to absorb the chlorophyll was agitated with the petroleum ether solution of chlorophyll. The sugar containing the precipitated chlorophyll was collected on top of a powdered sugar filter in a Buchner funnel. After washing the precipitate with petroleum ether, chlorophyll was eluted with purified ether, dried over anhydrous sodium sulphate and stored below 0°C. for use. Such ether solution[13] may be evaporated or diluted to attain the desired concentration of chlorophyll 'a' and 'b'.

For isolating chlorophyll 'a', the above solution containing the mixture was chromatographed under nitrogen in the usual manner over a column of powdered sugar. The chlorophyll 'a' band (easily recognized by its bluish colour) was isolated by extruding the column and mechanically separating the chlorophyll 'a' fraction. It was redissolved in ether and recovered. The ether solution was evaporated to the desired concentration and stored at 0°C.

For crude chlorophyll solutions, the original acetone solution after dilution was directly extracted with ether, washed, dried, evaporated to the proper concentration and stored below 0°C.

The powdered sugar was dried at 90°C. for 1 hour in a vaccum oven. The ethyl ether was purified by distilling first over anyhdrous calcium chloride and then over metallic sodium. Petroleum ether, cyclohexane, *n*-heptane, *n*-decane, decalin and mineral oil were purified by agitation twice with concentrated sulphuric acid, twice with fuming sulphuric acid and then with acidified permanganate solution, to free them from unsaturates. After this treatment they were thoroughly washed with distilled water, dried over anhydrous calcium chloride and finally distilled (petroleum ether, cyclohexane, *n*-heptane, and *n*-decane at atmospheric pressure and mineral oil under vacuum). The middle fractions were used in all cases. Cyclohexene and tetralin were left for several days over potassium hydroxide pellets and then fractionally distilled over potassium hydroxide by means of the Podbielniak column (cyclohexene at atomospheric pressure and tetralin under vacuum). The constant boiling fraction was employed for the experiments. Naphthalene was purified according to the standard methods.[10] Methyl and ethyl alcohols were distilled over a mixture of zinc powder and potassium hydroxide pellets. Cottonseed oil methyl ester was prepared through methanolysis in the presence of sodium methoxide followed by vacuum distillation of the methyl esters. Methyl oleate (iodine value, 84.3) and methyl linoleate (iodine value, 171.7, diene 0.15%) were obtained through the courtesy of the Hormel Foundation, U.S.A. The peroxide concentrates were prepared by means of contercurrent extraction, using the immiscible pair of solvents, petroleum ether and alcohol. Ethyl stearate was prepared by esterification of stearic acid[11] in the usual manner (benzene and ethyl aclohol and 2% concentrated sulphuric acid). In order to completely free the ethyl stearate from the oleate, the completely neutral stearate was subjected to hydrogenation in the presence of platinum catalyst [12] and then crystallized twice from ethyl alcohol solution.

Apparatus and Methods.—The low temperature bath consisted of an 18″ diameter jar fitted with a double-walled perforated annular tin vessel (Fig. 1) having an annular space

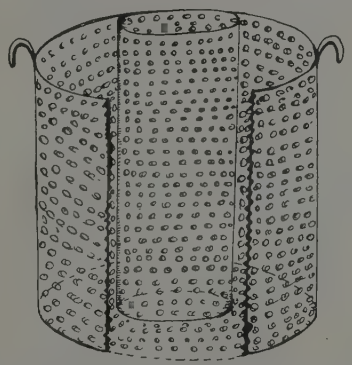

Fig. 1.—Perforated metal support for ice chips.

for holding ice chips and a clear 8″ diameter space in the centre. The perforations allow the brine solution to come in contact with ice, while leaving the central region undisturbed by ice. The bath medium in the middle is stirred by an efficient motor. By proper manipulation and 8-hourly addition of ice this bath could be maintained at a temperature between -4°C. and 0°C., while iced water could be used for temperatures between 10° and 18°C. The light from a 300 W. photoflood bulb (cooled in its housing by forced ventilation) passed through a plate glass window, the Pyrex glass bottom of the bath, and a 6″ layer of water before it reached the half litre three-necked Pyrex reaction flask. The flask was fitted with an inlet for dry oxygen or air (Corning fitted glass dispersion tube), a stirrer and an outlet provided with an anhydrous calcium chloride

absorption tube. The oxidation was carried out on 30% solutions of the substances in heptane, while hexane, cyclohexene, cyclohexane, tetralin, decalin, decane and the other solvents were employed as such (*i.e.*, 100% pure) when they were used alone during oxidation reactions. The oxidized material was freed of chlorophyll products by passing through a mixed column of charcoal and sugar[13] at 10-15°C. (ice-water jacket).

The solutions of chlorophyll (a + b) in different solvents, petroleum ether (b.p. 30°-60°C.), heptane, acetone, alcohol, ethyl ether and iso-octane (2.5 mg. per ml.) were left in stoppered Erlenmeyer flasks (cap. 250 ml. with 100 ml. solution, each) at 0°C., or close to it. The solutions were checked at intervals through observations on degree of changes in green colour and fluorescence of chlorophyll. The degree of stability of the chlorophyll led to the oxidation studies on heptane in the presence of chlorophyll at 0°C.

The cotton-seed oil mixed esters in heptane solution (30%) with chlorophyll (2.5 mg./ml.) was autoxidized in the absence of light by bubbling oxygen in a vessel covered with light-tight black paper. The photo-oxidations were conducted in a reaction vessel placed in the controlled temperature bath (Fig. 1), oxygen from a cylinder being bubbled through the reaction vessel. The peroxide number was determined for each substance at intervals by taking out aliquot portion of the substance autoxidized according to the well known methods published by Lundberg and Chipault.[16]

Results and Discussion

Chlorophyll (a + b) was found to be unstable in petroleum ether, heptane and acetone and alcohols, even at 0°C. It was found to be very stable in ether, with its green colour persisting for a long time, but the activity of chlorophyll in causing photo-oxidation falls off after six months or so at temperatures below 0°C. Ether used as solvent for storing chlorophyll at 0°C. was found to help the experimentations of shorter duration. Chlorophyll (2.5 mg./ml.) did not catalyze the oxidation of heptane even in two days at 0°C., but the chlorophyll changed colour to olive green. At 17-18°C., chlorophyll became bleached without much effect on the heptane. Consequently, it was thereafter used as solvent for oxidations involving other substances, fatty acid esters in particular. Purified iso-octane preserved the green colour of chlorophyll for over 3 days at 0°C. Iso-octane too is inactive towards oxidation by photo-sensitized chlorophyll at 0°C., indicating lack of reactivity by secondary H-atom during such reactions in contrast to ordinary autoxidation.

Without chlorophyll, the photo-oxidation of cottonseed oil mixed esters in heptane solution at 0°C. was not appreciable. At 17-18°C., it was also quite slow. In the absence of light, chlorophyll increased the stability of mixed esters three times. This may be attributed to the possible consumption of available oxygen in the formation of chlorophyll-oxygen complexes without involving energy transfer from the light that initiates oxidation. Thus the resulting lack of oxygen indirectly protects mixed esters.

Photochlorophyll oxidation of the unsaturated fatty acid esters proceeds at a rapid rate, much higher than that for ordinary photo-oxidation. This is brought out in Table 1 and Fig. 2, which

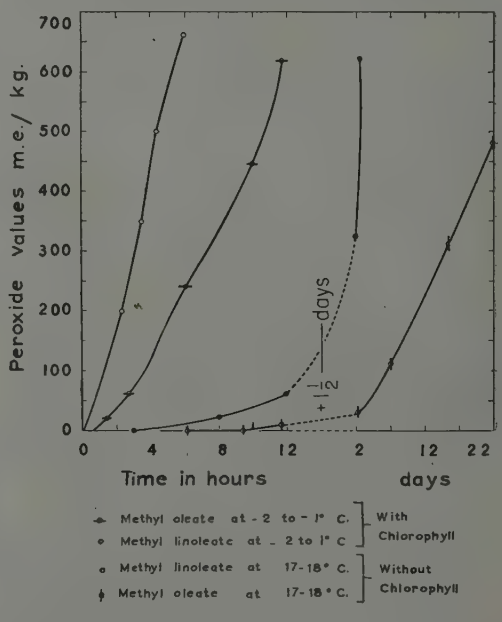

Fig. 2.—Photochlorophyll oxidation as methyl oleate and linoleate.

record with the progress of time, the peroxide values (indicating peroxide formation) of the two unsaturated materials under different conditions. Methyl linoleate has no induction period, whereas methyl oleate has definite induction period (about ¾ hr.) before initiation of oxidation in presence of light-sensitized chlorophyll. Plain

TABLE 1.—COMPARATIVE STUDIES ON PHOTO-OXIDATION IN THE PRESENCE AND ABSENCE OF CHOLOROPHYLL.

Methyl oleate				Methyl linoleate			
With chlorophyll -2 to -1 °C.		Without chlorophyll 17- 18 °C.		With chlorophyll -2 to -1 °C.		Without chlorophyll 17- 18 °C.	
Duration	P.V.	Duration	P.V.	Duration	P.V.	Duration	P.V.
1½ hrs.	20.0	6 hrs.	0.0	2¼ hrs.	199.0	3 hrs.	0.0
2½ „	62.0	9½ „	0.0	3½ „	350.0	8 „	19.0
4¾ „	234.0	11½ „	10.0	4¼ „	500.0	12 „	60.0
9 „	442.0	2 days	24.0	5¾ „	665.0	2 days	317.0
		7 „	107.0			2¼ „	618.0
11¾ „	614.0	15½ „	310.0				
		22 „	482.0				

photo-oxidation without chlorophyll shows for both substances induction periods during which the peroxide values increase extremely slowly. Light-sensitized chlorophyll has the advantage of greater resources of energy that make the oxidations go faster.

In another phase of the experiments, complete oxidation of methyl oleate and linoleate was attempted, and another aspect of photochlorophyll oxidation has thus been revealed by the data (Table 2). The initially slow oxidation of methyl oleate gradually increases in rate and finally keeps pace with methyl linoleate (Fig. 3). This may mean two things : (a) at the outset methyl oleate needs greater energy, not available from chlorophyll source, causing a slow rate, or (b) the energy-supply becomes sufficient in the later stages, indicating a more active form of chlorophyll. Such activated chlorophyll possesses an abundance of energy and the unsaturated fatty acid esters, methyl linoleate and oleate, could utilize only certian fractions of this energy (latter using probably greater) to rise to a maximum level of oxidation in each individual case, thereby equalizing the rates. In the same set of experiments under identical conditions, ethyl stearate did neither oxidize at 0 °C., nor at 17-18 °C., (Table 2 and Fig. 3). This confirms that the unsaturation and the related features of fatty acid esters are essential for the progress of photo-

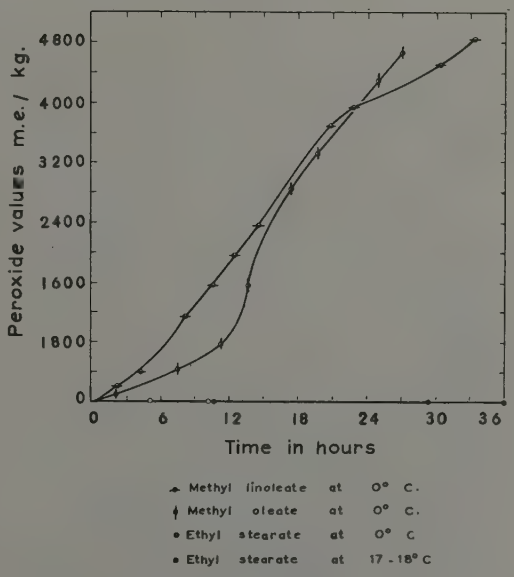

Fig. 3.—Comparative photochlorophyll oxidation of the saturated and unsaturated fatty acids esters.

oxidation. There is another significant phenomenon to be noted in these experiments. The accumulation of peroxides in both methyl oleate

TABLE 2.—PEROXIDE FORMATION DURING LIGHT-SENSITIZED CHLOROPHYLL OXIDATION.

Methyl oleate (0°C.)		Methyl linoleate (0°C.)		Ethyl stearate	
Time (in hrs.)	Peroxide number (m.e./kg.)	Time (in hrs.)	Peroxide number (m.e./kg.)	Time (in hrs.)	Peroxide number (m.e./kg.)
2½	54.0	2¼	200.0	(Temperature = 0°C.)	
7	405.0	4¼	500.0	5	0.0
11½	790.0	8¼	1130.0	10	0.0
13½	1460.0	10½	1560.0	Temperature = 17-18°C.	
17¼	2810.0	12½	1955.0	11½	0.0
19¾	3330.0	14½	2375.0	29½	0.0
25	4280.0	20¾	3655.0	36	0.0
27	4670.0	22¾	3920.0		
		30½	4600.0		
		33¼	4850.0		

and linoleate continued to the level of over p.v., 4500 m.e./kg. The ordinary oxidations [14–15] are not found to so much peroxides without further decomposition, which usually, carries on through free radicals produced by the main autoxidation reactions.[15] That there was no appreciable decomposition of peroxides in the photochlorophylly oxidation was shown by lack of absorption around 270 mμ in the products obtained from both methyl oleate and linoleate when autoxidized under light-sensitized chlorophyll. This observation suggests that the mechanisms of chlorophyll oxidation are quite different.

The importance of double bond and alpha-methylenic group at the same time for photochlorophyll oxidation is shown by oxidation studies on tetralene (alpha methylenic group and double bond, present), naphthalene (only double bond present) and decaline (fully saturated) in Table 3 and Fig. 4. As expected, the data in Table 3 indicate that photochlorophyll oxidation proceeded only with tetralene at 0°C. and other substances resisted such oxidation. The negligible effects of oxidation on decaline at 17-18°C. may perhaps be due to impurities. Fig. 4 shows the rather remarkable progress of oxidation in case of tertralene.

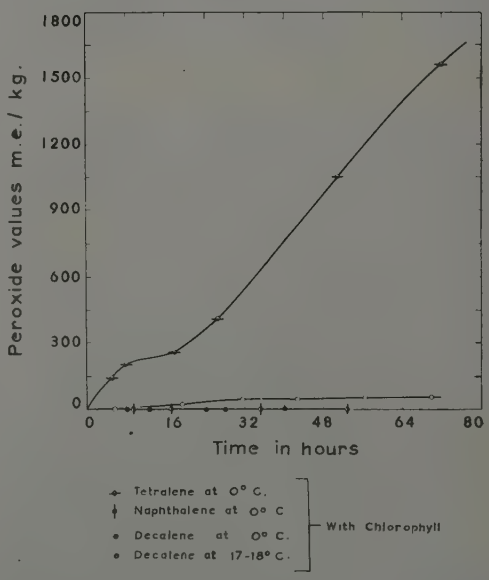

Fig. 4.—Photochlorophyll oxidation of certain specific chemicals : tetralene, naphthalene and decalene.

TABLE 3.—THE ROLE OF ALPHA METHYLENIC GROUP IN PHOTO-CHLOROPHYLL OXIDATION.

Tetralene (0°C.)		Naphthalene (0°C.)		Decalene	
Time (in hrs.)	Peroxide number (m.e./kg.)	Time (in hrs.)	Peroxide number (m.e./kg.)	Time (in hrs.)	Peroxide number (m.e./kg.)
6	150.0	10	0.0	(Temperature = 0°C.)	
8½	170.0	17½	0.0	8, 12, 24	0.0
18½	240.0	35½	0.0	28, 40	
26¼	390.0	52½	0.0	17 — 18°C.	
50½	1010.0			6	0.0
72½	1570.0			19	12.0
				31½	28.0
				42	25.0
				56½	25.0
				70½	26.0

The foregoing results indicate that the alpha methylenic group in conjunction with its adjacent double bond forms complex with chlorophyll under sensitization by visible light. Such chlorophyll complex (reducing) would then interact with similar chlorophyll-oxygen complex (oxidizing) to form hydroperoxides and original chlorophyll, as described in the introduction. Moreover, this property of complex formation is not appreciably affected by the presence of other pigments in the leaves (xantophylls, carotenes, etc.).

Further work directed towards an exposition of the mechanisms of chlorophyll oxidation in the presence of visible light is in hand.

Acknowledgement

The author wishes to thank Dr. M. Qudrat-i-Khuda and Dr. Salimuzzaman Siddiqui, for their interest and encouragement in the pursuit of this problem. He is also grateful to the Dacca Univeristy authorities for offering many research materials needed in the present study, and to Mr. Waziullah and Mr. H. C. Das for assistance in part of this work.

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QUANTITATIVE AND STRUCTURAL ANALYSIS OF KALABAGH IRON ORE BY PHYSICO-CHEMICAL METHODS WITH REFERENCE TO ITS BENEFICIATION

Part III.—X-ray Analysis of the Component Mineral Phases

MAZHAR MAHMOOD QURASHI, SADRUL HASAN RIZVI AND M. LATIF AHMAD

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

Introduction

In the previous communications [1,2] of this series, analytical data have been given for random samples as well as specially collected representative samples of iron ore from the Kutch Khurtop mining property in Kalabagh. The results obtained by the chemical and physical methods agreed to within less than 1%, and a synopsis of the more significant data is given in Table 1. The iron content was found to vary from 22.4% to 39.2% for the representative samples drawn out from the various parts of the ore body. With reference to these figures it is noteworthy that the hand-picked sample from the area of the ore field leased out to Mr. Abdul Karim has 54% iron content. The analyses also point to the presence of nearly 25% of ferrous carbonate, but do not give any indication of the various structural forms in which the rest of the iron occurs. Such a structural study has now been carried out, and is described below. It has confirmed the presence of $FeCO_3$ and has further resulted in establishing the occurrence in appreciable quantities of three other ferruginous phases, namely chamosite, limonite, and hematite, all of which have an important bearing on the plan of beneficiation of the ore and its smelting, which are to be discussed in Part IV of this series of communications.

X-ray Patterns of the Five Main Samples

The X-ray diffraction technique has been employed as the one most suited to such structural studies, and powder patterns of the five typical samples taken with an 11.4 cm. diameter camera using filtered chromium $K\alpha$ radiation are shown in Fig. 1. It is significant that the "mean" and the "middle" samples, both of which contain nearly 34% iron, have almost identical patterns, while those of the other three show striking differences. Also, the large number of lines in the patterns suggests the existence of several important component structures corresponding to different chemical compounds or minerals. For the identification of these minerals, we must make a comparison with corresponding patterns of known standards, so as ultimately to account for all the observed lines, which are given in Table 2 along with their estimated intensities.

The preliminary identification was done by comparing the d-values of the strongest lines of the patterns with those given in the A.S.T.M. X-ray Data Cards[3] and also with those of a standard pattern of α-Fe_2O_3. This comparison showed that some hematite (α-Fe_2O_3) is present in all the samples whose patterns appear in Fig. 1. Three important pairs of lines characteristic of this mineral

TABLE 1.—SYNOPSIS OF ANYALYSES OF IRON ORE SAMPLES FROM KUTCH KHURTOP MINING AREA.

	Poorest sample	Richest sample	Middle sample	Mean Dump sample	From A. Karim's property
Iron %	22.4	39.2	34.7	33.5	54
Al_2O_3%	...	11.0		13.0	
Total Si O_2%	..	15.2		24.2	
CaO%	2.3	3.5		1.1	
CO_2%	6	6		11	
H_2O%	5	6		2	

TABLE 2.—d-VALUES IN ANGSTROMS AND ESTIMATED INTENSITIES OF THE LINES DOWN TO 1.3 A.U. IN THE OBSERVED POWDER PATTERNS OF THE FIVE TYPICAL SAMPLES OF IRON ORE.

s=strong ; m=medium ; w=weak ; f=faint ; d=diffuse.

A. Karim's sample	Mean sample	Middle sample	Richest sample	Poorest sample
	m 7.20	w 7.25		m 7.20
*f 6.95	s 6.98	s 6.90	s 7.0	m 7.00
				m 6.00
			f 4.60	
				f 4.40
				f 4.35
*f 4.20	f 4.15	f 4.20	s 4.15	f 4.25
f 3.68	f 3.67	f 3.65		w 3.63
	m 3.58	w 3.60		
	m 3.51	w 3.55	m 3.50	w 3.53
	f 3.33	w 3.32		
				m 3.14
**f 3.05	f 3.09			
*f 2.80	s 2.80	s 2.80	f 2.80	
s 2.70	s 2.69	m 2.69	m 2.70	s 2.70
				f 2.55
s 2.50	s 2.52	s 2.50	m 2.52	s 2.50
*w 2.45	w 2.44	w 2.45	m 2.45	
	w 2.35	w 2.34		s 2.33
			f 2.25	
w 2.20	f 2.19		f 2.18	m 2.20
	m 2.14	s 2.12	f 2.13	
	m 1.96	m 1.96		
				s 1.86
m 1.83	w 1.84	w 1.83	f 1.82	s 1.85
		f 1.78		f 1.76
	m 1.737	s.d 1.725	w.d 1.730	
*f 1.710	w 1.715			
s 1.690	m 1.695	m 1.685	w 1.680	s 1.685
				m 1.655
	f 1.635			
m 1.595	f 1.596			w 1.595
*f 1.555	s 1.560	s 1.555	m.d 1.560	
	w 1.535			
	w 1.523	f 1.520	w.d 1.520	
*f 1.515	w 1.506	f 1.505		
s 1.485	m 1.488	m 1.490	f.d 1.475	s 1.485
s 1.450	m 1.458	m 1.450	f.d 1.450	s 1.450
*f 1.425	w 1.435	w 1.425	f.d 1.430	w 1.435
				f 1.395
	f 1.380	f 1.380		w 1.385
	f 1.375	f 1.375		
f 1.350				
	f 1.325			
w 1.310	f 1.310			s 1.310

* This denotes lines not due to hematite in the pattern of the sample from Mr. A. Karim's lease. These are comparatively faint and agree with the strongest lines of siderite, limonite and chamosite.

** Possibly due to chalcopyrite.

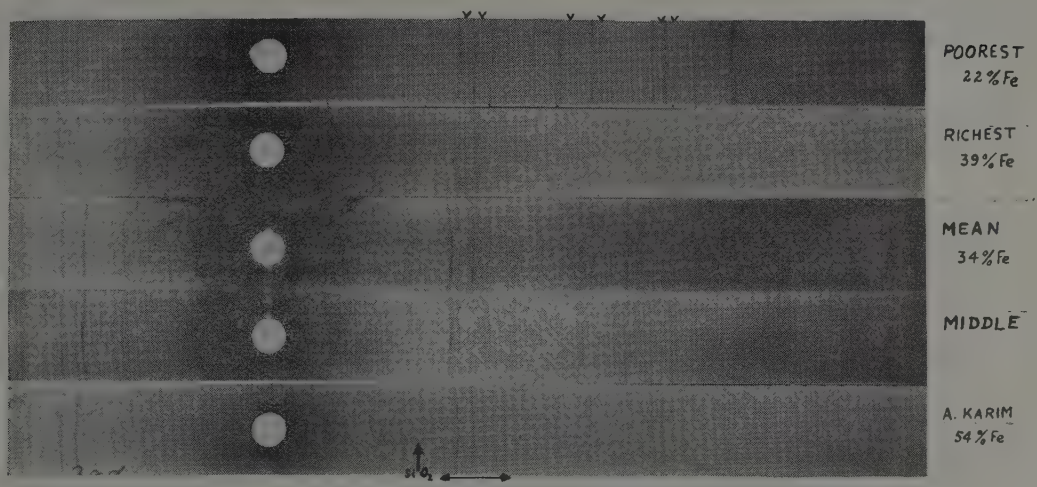

Fig. 1.—X-ray powder diffraction patterns of the five typical samples of Kalabagh iron ore, showing the complexity of the mean and middle samples; the only line due to quartz is marked SiO_2 with a vertical arrow (patterns taken with Cr K α filtered radiation). The region marked ←→ shows strikingly the differences between the various patterns.

are marked with a "V" in the figure, and they can be seen in all the five patterns, although with different intensities. The pattern labelled "A. Karim" appears to be largely hematite because the intensities of all lines not due to hematite are very low in its pattern. This result is consistent with its high iron content (54%), because iron ores containing more than 50% iron consist mostly of the oxides of iron.

Identification of the Different Component Structures or Mineral Phases

(*a*) *Components of the Mean Sample.*—A search through the A.S.T.M. cards indicates that, in addition to hematite, the mean sample contains siderite ($FeCO_3$), chamosite (a ferruginous alumino-silicate usually containing 24 to 32% iron), and limonite ($Fe_2O_3.H_2O.nH_2O = 2FeO(OH).nH_2O$). Confirmation of this is obtained by direct comparison with standard powder patterns as shown in Table 3 and Fig. 2, where the patterns of hematite (α-Fe_2O_3), siderite and chamosite are placed alongside that of the mean representative sample, the resolved lines of chamosite being marked with arrows. It is seen that the siderite and hematite contributions to the pattern are of about equal intensity, thus indicating that the ore contains roughly equal quantities of the heavy atom (iron) in these two minerals. Taking their iron contents as 69% and 48% respectively, this gives a ratio of about 2:3 for hematite and siderite. About half a dozen lines remain outstanding after the siderite and hematite lines have been accounted for, and most of these can be correlated with the stronger lines of chamosite, while the inner line of the strong low-angle doublet (d=7.1 A.) is probably due to kaolinite, two other lines of which appear somewhat indistinctly in our patterns. A weak spotty line (marked "SiO_2" in Figs. 1 and 2) corresponding to the strongest quartz line is observed at 3.33 A. The contribution of the chamosite lines to the intensity of the whole pattern is also of the same order as that of siderite and hematite, whence we conclude (by an argument similar to the previous one) that these three minerals occur in the mean sample in the ratios of 2:3:4 approximately.

(*b*) *Components of the Richest Sample (39% Iron.)*—The X-ray patterns of the richest and poorest samples are both strikingly different from that of the mean sample in that the lines of siderite ($FeCO_3$) are absent, its strongest line at 2.80 A, (just inside the first strong doublet of α-Fe_2O_3) being hardly detectable in the pattern of the richest sample (Fig. 1). Since the iron content is higher than the average, it follows that a large part of the iron must be present here in still another form, and the strong line just outside the first α-Fe_2O_3 doublet appeared to belong to this new phase. After a thorough search, it was found that this phase is limonite ($Fe_2O_3.H_2O.nH_2O = 2FeO(OH).nH_2O$), a somewhat diffuse pattern for which is shown alongside of the pattern of the richest sample in Fig. 3. This diffuse pattern of limonite was actually obtained when attempting

TABLE 3.—COMPARISON OF X-RAY POWDER LINES DOWN TO 1.3 A. U. FOR THE VARIOUS IRON ORE SAMPLES WITH STANDARD DATA ON SIDERITE, HEMATITE, CHAMOSITE, LIMONITE, KAOLINITE AND BOHIMITE.

s=strong (50—100) ; m=medium (20—50) ; w=weak (10-20) ; f=faint (less than 10) ; d=diffuse ; faint lines in the standard pattern have been omitted. Almost all the lines of the limonite pattern in Fig. 3 are diffuse.

Mean sample	Siderite	Hematite	Chamosite	Limonite		Richest sample	Poorest sample	Kaolinite	Bohimite
				ASTM cards	Fig. 3				
m 7.20							m 7.20	s 7.15	
s 6.98			s 6.94			s 7.0	m 7.00		
							*m 6.00		s 6.11
			s 4.64			f 4.60			
							f 4.40	m 4.45	
							f 4.35	s 4.35	
f 4.15				s 4.18	s 4.20	s 4.15	f 4.25	s 4.17	
								m 4.12	
								m 3.84	
f 3.67		s 3.68					w 3.63	w 3.73	
m 3.58	m 3.61				f 3.60			s 3.57	
m 3.51			s 3.51			m 3.50	w 3.53		
f 3.33				m 3.39				m 3.37	
							*m 3.14	w 3.14	s 3.164
f 3.09		(w 3.01)						w 3.09	
s 2.80	s 2.80	(f 2.79)	m 2.78			f 2.80			
s 2.69		s 2.69	w 2.69	s 2.69	s 2.69	m 2.70	s 2.70	w 2.75	
				m 2.58	f 2.59		f 2.55	s 2.55	
s 2.52		s 2.51	s 2.51			m 2.52	s 2.50	m 2.52	
w 2.44				s 2.45	s 2.45	m 2.45		s 2.486	
w 2.35	w 2.36							s 2.374	
							*s 2.33	s 2.331	s 2.346
				m 2.25		f 2.25		s 2.284	
f 2.19		s 2.20		s 2.19	m 2.20	f 2.18	m 2.20	m 2.182	
m 2.14	w 2.13		m 2.13			f 2.13		w 2.127	
m 1.96	w 1.96							s 1.985	
								m 1.935	
							*s 1.86	w 1.892	m 1.860
w 1.84		s 1.837		w 1.83		f 1.82	*s 1.85	m 1.825	m 1.850
			m 1.77				f 1.76	s 1.778	
m 1.737	m 1.73			s 1.72	m 1.725	w.d 1.730			
w 1.715									
m 1.695		s 1.691		w 1.69		w 1.680	s 1.685		
f 1.635							m 1.655	s 1.659	w 1.662
f 1.596		m 1.596		w 1.60			w 1.595	s 1.616	
								m 1.581	
s 1.560			s 1.56	s 1.56	m 1.570	m.d. 1.560			
w 1.535			m 1.53					s 1.539	
w 1.523					m 1.525	w.d. 1.520			
w 1.506	w 1.50			m 1.51					
m 1.488		s 1.484	w 1.48			f.d. 1.475	s 1.485	s 1.486	
m 1.458		s 1.451		m 1.45	m 1.460	f.d. 1.450	s 1.450		w 1.453
w 1.435			w 1.43				w 1.435		
				w 1.42	m 1.425	f.d. 1.430			
				w 1.40			f 1.395		
f 1.380							w 1.385		
f 1.375									
		w 1.348							
f 1.325				w 1.32					
f 1.310		m 1.309					s 1.310		w 1.312

Note : The weak doublet given in parantheses in the hematite pattern is produced by the K β radiation (passing through the filter) and corresponds to the strong K α doublet at 2.6 ± 0.1 A.

* Denotes lines in the pattern of the poorest sample that are accounted for by the bohimite pattern only.

to take an X-ray powder pattern of $FeCO_3$. It was found after several attempts that the carbonate invariably changed into the hydrated oxide, and the diffuseness of the lines in Fig.3 is probably due to the incompleteness of the transformation. This phenomenon also suggests that the limonite in the richest sample may have resulted from decomposition of siderite. The replacement of CO_2 by OH in the process would result in a loss of weight and therefore an increase in percentage iron content. The pattern of the richest sample is also remarkable for the fact that two comparatively weak lines of chamosite that overlap with other patterns in Fig. 2 are here clearly resolved,

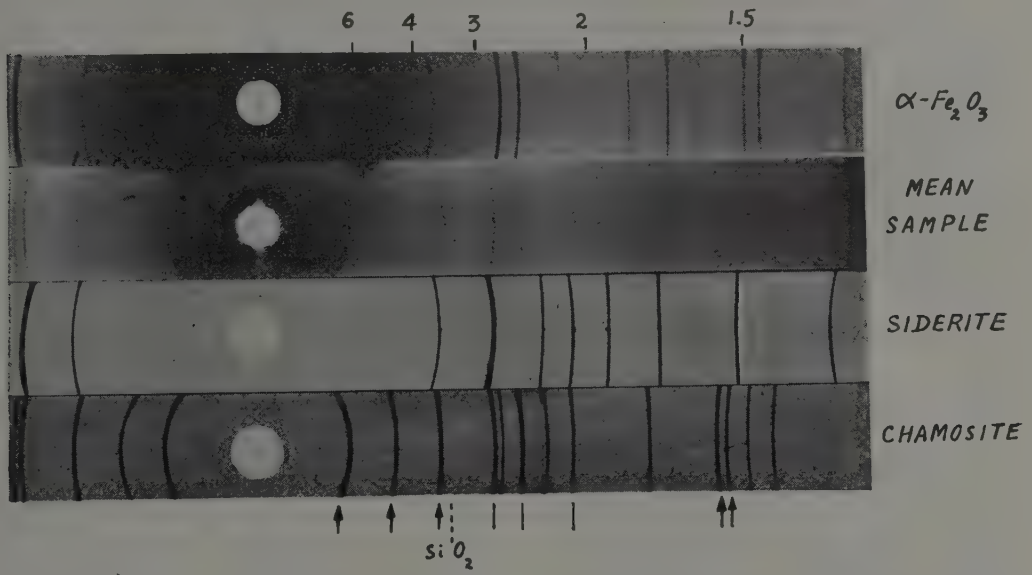

Fig. 2.—Comparison of the powder pattern of the mean sample with those of its constituent minerals, the arrows indicating the resolved lines due to chamosite. The patterns of siderite and chamosite have been made up from the standard data in the A.S.T.M. cards, the thicknesses of the lines being roughly proportional to the intensities. The scale at the top indicates d-values in Angstrom units.

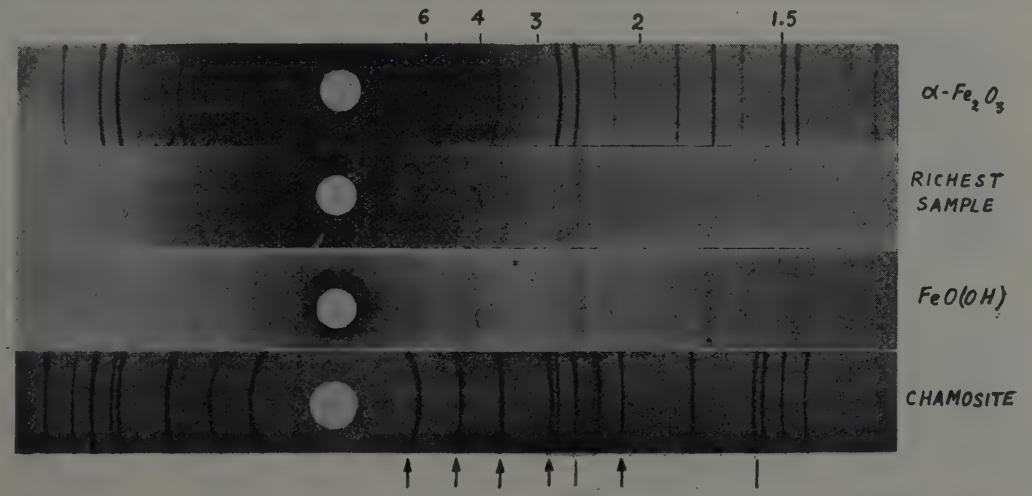

Fig. 3—Comparison of the pattern of the richest sample with those of its constituent minerals, showing the replacement of siderite by limonite. The arrows indicate the resolved lines of chamosite. The scale at the top indicates d-values in Angstrom units.

as shown by the arrows in the 2-3 A. region. A detailed comparison of the lines of the patterns is given in Table 3, which moreover shows that the strongest lines of limonite are also to be found in the pattern of the mean sample, although with a very low intensity, corresponding to a limonite content of about half that of the hematite.

(*c*) *Components of the Poorest Sample*.—The X-ray pattern of the poorest sample contains several strong lines (marked with an asterisk in Table 3) not accounted for by any of the mineral phases referred to above. Reference to the A.S.T.M. cards showed that they are due to bohimite (α-$Al_2O_3.H_2O$), and this is clearly brought out by the comparative patterns shown in Fig. 4, which also shows the presence of unaccounted lines at 7.1 A and the 4.3 A group of lines. These lines can be identified as being due to kaolinite, as shown in the table.

Estimated Mineral Composition of the Samples

From the foregoing analysis, it can be concluded that kaolinite, chamosite, and hematite are present in all the samples examined, and from the intensities of their characteristic patterns, their relative proportions can be estimated. The pattern marked "A. Karim" shows only traces of siderite, limonite and chamosite, so that over 75% of the iron must be present as hematite. This type of ore would be excellent for treatment by a simple beneficiation and smelting process, but it does not appear to be available in large quantities.

An accurate quantitative estimate of the kaolinite and bohimite in the mean sample is difficult to make from the X-ray data, and a figure of $10\% \pm 5\%$ is the best that can be obtained from the two or three weak lines available. If we allow another 10% for the free silica (noted above) and the traces of compounds of titanium, chromium, strontium and zirconium found in the X-ray spectrometer record (Part II, Fig. 1), we find that the ferruginous compounds, limonite, hematite, siderite, and chamosite, together make up 80% of the mean sample. Since these four minerals have been shown above to be present in the approximate ratios of 1:2:3:4, respectively, we immediately get the percentages given in the second column of Table 4. The next column gives the final estimates of composition, corrected so as to give a total iron content of 34%, while the last column shows the contribution of each phase to the iron content.

Subsequent to the completion of the foregoing analysis, the results of mineralogical analyses on the representative sample were made available to the authors through the courtesy of Mr. H. R. Amundsen of the National Planning Board of Pakistan. These analyses were carried out in the Hoganas Laboratories in Sweden, and their results are summarized in Table 5, in which the last column shows the estimated contributions of the various phases to the iron content. Comparison

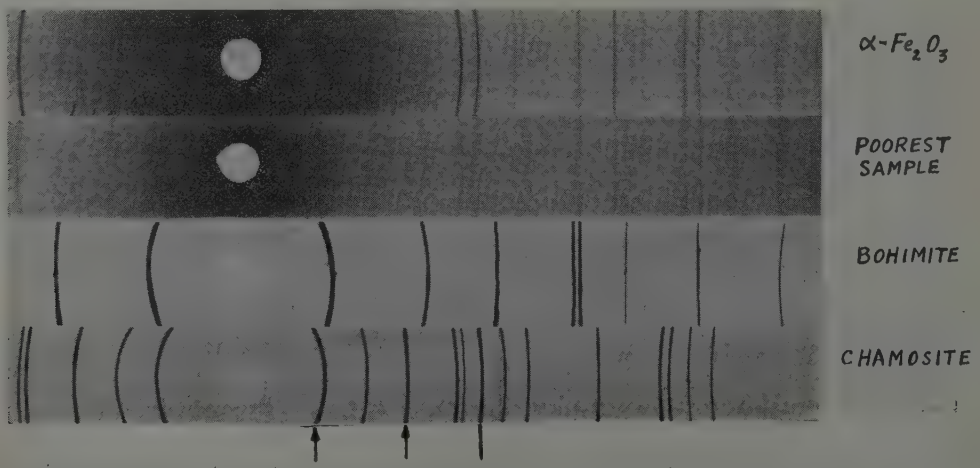

Fig.4.—Powder patterns showing the presence of bohimite, chamosite and hematite in the poorest sample. The pattern of bohimite (like that of chamosite) is made up from the standard data.

TABLE 4.—PERCENTAGE MINERAL COMPOSITION OF THE MEAN SAMPLE BY X-RAY ANALYSIS.

Constituent minerals	Weight % from X-ray analysis	Corrected values	Contribution to iron content
Limonite ($Fe_2O_3.H_2O.nH_2O$)	8	7	4·5
Hematite (α–Fe_2O_3)	16	14	9.8
Siderite ($FeCO_3$)	24	22	10.6
Chamosite* 3 (Fe, Mg)O.Al_2O_3.2 Si O_2.nH_2O ..	32	30	8.4
TiO_2,Cr_2O_3 etc.	5	6	<1
Quartz	5	6	—
Kaolinite, bohimite	10±5	15	—
Total	100	100	33.8±0.5

* Chamosite is a ferruginous clay, and the formula given is therefore only approximate. It may contain 24–32% iron, and an average figure of 28% has been used in the table above.

of Tables 4 and 5 shows that in the main the results of the mineralogical analysis are in fair agreement with those of the X-ray analysis when allowance is made for the variability of the ore samples. However, there is a significant difference in that, on the basis of the analysis presented in this paper, a separate estimation of the limonite and the hematite can be made, whereas in Table 5 there is no reference to hematite, while the %given for the limonite indicates that both the hydrated and unhydrated forms of the oxide are included in that value. Another difference is that the aluminous sediments (corresponding to kaolinite and bohimite in Table 4) appear to have been underestimated in Table 5. These discrepancies are attributable partly to the difficulties inherent in the chemical method of analysis, and partly to the fact that for the present investigation several samples from different levels of the ore field were available, two of which (Figs. 3 and 4) were particularly rich in limonite and bohimite, respectively, thus facilitating their identification and estimation.

TABLE 5.—MINERALOGICAL ANALYSIS OF MEAN REPRESENTATIVE SAMPLE.

Constituent minerals	Analysis by Hoganas, Sweden	Contributions to iron content
Limonite ($Fe_2O_3.nH_2O$)	24.9	14.0±2
Hematite (Fe_2O_3) ..	..	..
Siderite ($FeCO_3$) ..	25.6	12.3
Chamosite	35.6	9.0±0.5
Ilmenite ($FeO.Tio_2$) ..	1.7	0.6
Quartz	5.1	..
Residue (aluminous sediments)	7.7	..
Total ..	100.6	35.9±2
Total iron by analysis=35.8%		

Decomposition of the Carbonate

When the siderite ($FeCO_3$) is completely decomposed (*e.g.*, by weathering) to give limonite [$Fe_2O_3H_2O=2FeO(OH)$], there is a loss in weight of 24% on the weight of siderite. This should therefore raise the percentage weight of iron in the sample by a factor of 100/(100–24×0.24) = 100/(100–6). The iron content calculated on this basis is 35.5%, thus only partly explaining the 39.2% of iron in the richest sample, which most probably also contains a higher percentage of the richest phase, hematite, than does the mean sample. In this connection it was of interest to study the decomposition of the carbonate by simple roasting at various temperatures. Fig. 5 shows comparative X-ray powder patterns of various portions of the mean sample heated for half an hour in an oven at three different temperatures, namely 450°C., 600°C. and 800°C.

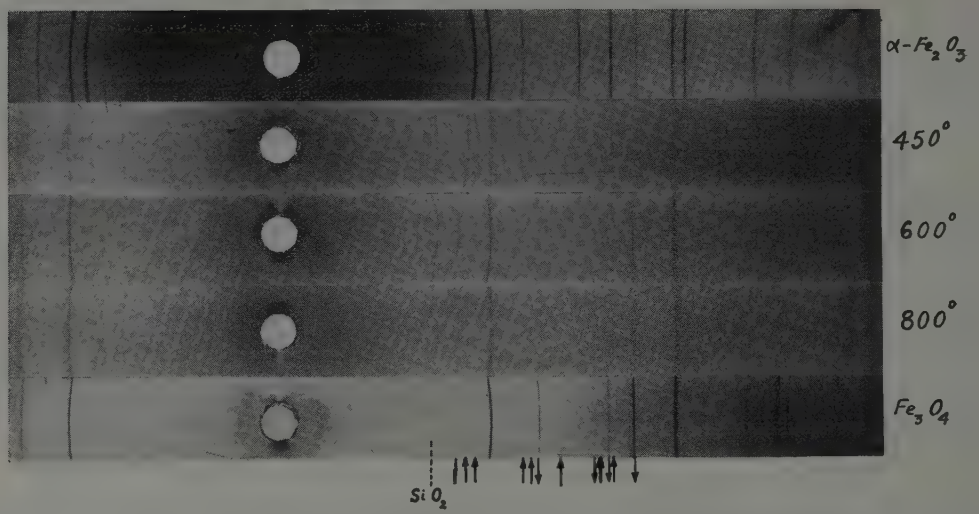

Fig. 5.—Powder patterns of roasted samples of ore compared with those of α-Fe_2O_3 and Fe_3O_4. The direction of the arrows indicate increasing intensity of the corresponding lines, and they show the progressive replacement of the hematite, limonite and siderite lines by those of Fe_3O_4 as the roasting temperature is raised (patterns taken with Cr K α filtered radiation).

The heat treatment at 450°C. has produced a barely detectable weakening of the siderite lines in the pattern, thus showing that very little of it is decomposed at this temperature. The patterns obtained after roasting at 600°C. and 800°C., on the other hand, show the gradual disappearance of the lines of both siderite and hematite and their replacement by the lines of the magnetic oxide, Fe_3O_4 (and γ-Fe_2O_3), whose pattern is shown in the bottom of Fig. 5. Some typical lines that increase in intensity as we go from the top to the bottom are marked in the figure with arrows pointing downwards, while the disappearing lines of the initial phases are marked with arrows pointing upwards. A particularly interesting feature of Fig. 5 is that the pattern of chamosite also undergoes considerable modifications even at 600°C., which suggests the desirability of further study of roasting as a likely means of beneficiation of this ore.

Conclusions

(a) The ore from the Kutch Khartop area contains about 50% of the iron oxides and ferrous carbonate, and more than 30% by weight of the ferruginous alumino-silicate, chamosite. The fine dissemination of the chamosite throughout the ore is likely to make its efficient beneficiation a complex process, unless hand-picking yields ore with a significantly lower chamosite content.

(b) Beneficiation by simple roasting or a modified roasting procedure presents an interesting possibility.

(c) Chemical treatment such as leaching etc. may have to be resorted to for the complete recovery of the iron from the ore. Since the ultimate choice of steel-making plant is likely to be governed by the economics of such beneficiation processes, their detailed study is in hand and the results will be reported in Part IV of this series of communications.

Acknowledgements

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DESIGN OF A SIMPLE URANIUM-THORIUM DISCRIMINATOR FOR WEAKLY ACTIVE ORES CONTAINING LESS THAN 1% U_3O_8 EQUIVALENT

Part I.—Study of the Self-Absorption of the β and γ Rays in Relation to Optimum Sample Thickness and Discrimination

KHURSHID HUSAIN, MOHAMMAD AZEEM,* NURUL AHMED AND MAZHAR MAHMOOD QURASHI

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

1. Introduction

In the initial stages of the radioactive assay of mineral samples, the two most important questions to be answered are (a) what is the major radioactive constituent and (b) what is its percentage concentration in the sample. For relatively rich ores, a semi-quantitative chemical assay can be carried out, but these methods are always tedious and, for concentrations of less than 2 or 3%, precise results are often difficult to obtain due to interference from silica and iron.[1] Therefore, it is of great practical utility to develop physical methods of analysis. One of the most useful methods uses the characteristic X-rays excited in the elements composing the mineral. This method however suffers from two drawbacks, (a) the lower limit to the sensitivity is in the region of 0.05 to 0.1% uranium or thorium, and (b) interference from the K-lines of rubidium, yttrium, and zirconium (for uranium) and rubidium and bromine (for thorium) is serious if any of these elements is present in quantities greater than 10%. A method involving the estimation of radon,[1] and two methods using electronic discrimination[2] between (a) particle energy and (b) the half life of radium C′ and thorium C′, have been suggested but are rather complicated in application.

A powerful and accurate method is that of β-ray spectorgraphy, by which the energies of the γ-spectra of the active nucleii can be measured and thence the elements identified. The apparatus is elaborate, and quantitative data are obtainable after considerable time and trouble. The discrimination obtained is very high, because no two elements give the same γ-ray spectrum, but such high discrimination is not essential for the survey of minerals, because there one is looking primarily for uranium and thorium, while interference can be expected from the radioactive isotope of potassium.

2. Principle of the Simple Method

By sacrificing the excessive discrimination of the β-ray spectrograph, and reducing the examination to a simple analysis by absorption of the emitted β and γ-rays, we obtain a simple means of identifiying thorium and uranium, and of estimating their relative concentrations. Ideally, if potassium is assumed to be absent, two measurements of the total $(\beta + \gamma)$ counts through two suitable thicknesses of absorbing matter should provide the necessary discrimination between thorium and uranium. This technique is already employed in a type of discriminator and gives satisfactory results for rich ores. However, for the poor ores, the absorption in the samples itself becomes considerable, and must be allowed for.

The present development consists in making use of the mineral sample as its own absorber and in selecting the two thicknesses so that the smaller thickness, d_β, is of the order of the β range, and the larger thickness, d_γ is of the order of the γ-range in the powdered mineral. This has the advantage of making the ratio n_γ/n_β of the γ to the β counts more favourable for accurate measurement and discrimination than the ratio of γ counts through two different thicknesses suggested by Behounek.[1] Figure 1 shows two possible

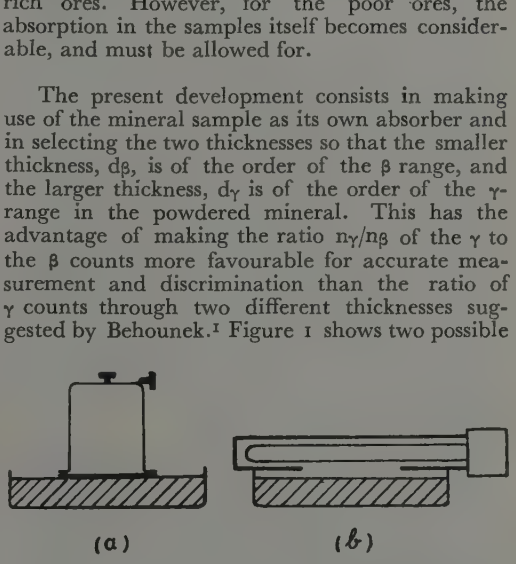


Fig. 1.—Two possible arrangements for investigating the variation of the counting rates with sample thickness using (a) an end window counter (left) and (b) a tube counter (right).

experimental arrangements, where either the end-window or the tube type of Geiger Muller counter measures the total counts due to the β and γ radiations from any one thickness of sample. If a substance gave off β-rays only, the plot of the counting rate n_β against thickness ' d ' would be somewhat as in Fig. 2 (a), but when only γ-rays are given off, the curve is as shown in Fig. 2(b)

* Present address: Atomic Energy Commission, Karachi.

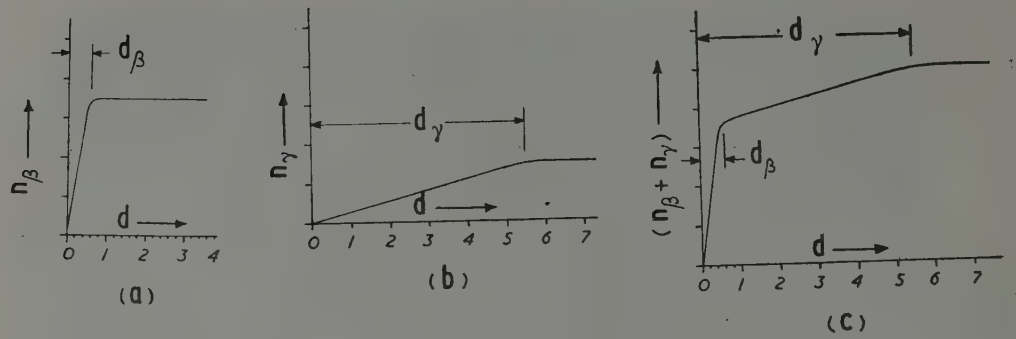


Fig. 2.—Idealized representation of variation of counting rate with sample thickness for (a) unique energy beta emitter, (b) unique energy gamma emitter, and (c) combination of both emissions.

where d_β and d_γ may be called the ranges of the β and γ-rays, respectively . When both these emissions are combined, we get Fig. 2 (c). For a unique energy of the β-rays and a simple γ-ray line, the plot should consist of two inclined straight lines, the first and steep one corresponding essentially to the β-rays and the second one to the γ-rays. The bend between the two occurs at a thickness corresponding to the range of the β-ray. The second part of this graph reaches saturation at a much larger value of thickness, corresponding to the large range of the γ rays. Since the actual β and γ-ray spectra of radioactive substances are complex, especialy when accompanied by decay products, each of the two straight lines of Fig. 2(c) will be slightly curved, being in fact made up of a series of lines, each terminating at the vlaue of d corresponding to the range of a particular group of β or γ-rays. This presents the possibility of a definite discrimination between different radio-active emitters by determining the shapes of these curved lines, thus making in effect an absorption spectrograph.

Such a detailed analysis would of course require accurate measurements of the counting rate with a whole series of graded thicknesses of sample. In the present communication , such an analysis of the β and γ-ray counts from uranium, thorium, and potassium is presented and the necessary conditions are determined for (a) efficient discrimination between them, and (b) accurate estimation of the quantities of the three metals in any given sample. On the basis of these results, the essential features of a combined discriminator-estimator are worked out, detailed tests on which form the subject matter of Part II of this paper.

3. Experimental Details

(*a*) *Preparation of Standards.*—The standard samples were prepared by successive dilution of the active material with dry calcium carbonate. The dilutions were carried out in stages, with thorough mixing at each stage, the concentration being reduced by a factor of 5 to 10 in each stage. The four standards used contained : (i) 0.060% of uranium in equilibrium (from analysed low-grade pitchblende), (ii) 0.50% thorium nitrate (prepared about five years ago), (iii) 30% potassium chloride (*i.e.*, 16% potassium) in calcium carbonate, and (iv) 0.255% of uranium in the form of chemically separated uranyl nitrate. The fourth standard was used to study the effect of lack of equilibrium in the uranium series.

(b) *Measurement of Counting Rate.*—Various quantities of the material under examination were taken in a 9 cm. diameter flat-bottomed petri dish, across the top of which a Geiger Muller tube counter* was held, the surface of the tube being about 4 mm. above the top of the dish. The counting rate was measured by noting the number of counts recorded by a Dynatron Scalar Unit in ten to twenty successive intervals of one or two minutes. Since a suitable lead castle was not available, the back-ground rate of the counter had to be determined when similarly placed, but without any sample in the petri dish. This back-ground rate was measured at the commencement and also at regular intervals all through the experiment. By subtraction, the total $(\beta + \gamma)$ counts, $n\beta + n\gamma$, recorded by the counter for any one quantity of material in the petri dish were obtained. The mean mass per unit area of the sample was obtained from its weight and the diameter of the dish, and this could be correlated with the thickness, which was measured correct

* The tube counter was a Frieseke and Hoepfner beta-gamma Geiger Muller tube (No. FHZ 69) with an operating plateau voltage of 700 volts.

to 0.2 mm. with a travelling microscope. This correlation is shown in Table 1, which also gives the γ and β+γ counting rate for various thicknesses of the uranium (pitchblende) standard. Since the petri dish was only 1.5 cm. high, some modification was necessary for working with larger thicknesses of material, going upto 8 cm. A dish of adjustable height was improvized by surrounding the petri dish with a stout well-fitting cardboard cylinder 10 cm. in height. By supporting the dish on a wooden block and sliding the cardboard cylinder up and down, various thicknesses of material upto 8 cm. could be used satisfactorily. During these experiments, the counter tube was placed so that its lower surface was about 4 mm. above the (upper) flat surface of the material being tested, in which position the β-shield just rested on top of the cardboard cylinder.

Since the area of the petri dish and therefore of the cylinderical sample is fixed, the effect on the counter of the rays from a particular layer will depend on its distance, x, from the counter (Fig. 3). The variation with x is complex, and in order to minimize this variation, the slotted metal β-ray shield was retained on the counter tube, thus constituting an opening of fixed angular width for the β rays. For depths of several centimetres, this angular spread falls within the diameter of the petri dish, and therefore the correction for distance may be neglected.

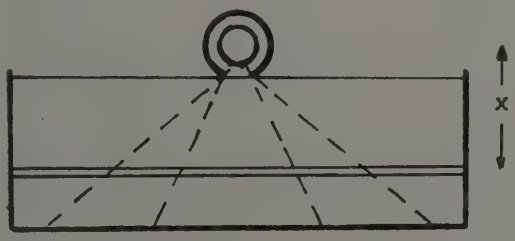


Fig. 3.—Schematic representation of the effect of counter shield with slotted opening.

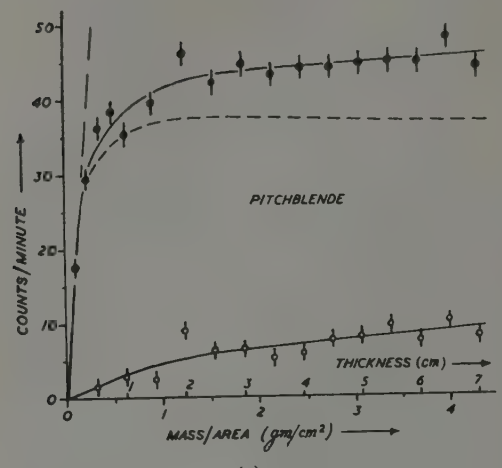
4. Measurements with Standards and their Interpretation

The β+γ rates combined, *i.e.*, $n\beta + n\gamma$, were measured upto a thickness of 1 cm. in steps of 0.2 cm. and then in steps of 0.5 cm. upto the maximum used in the particular experiment. The γ-counting rate $n\gamma$ was measured all along at intervals of about 0.5 cm., the background counts being separately measured with closed β-shield and corrected for. The results of the measurements with the picthblende standard are shown graphically in Fig. 4(a), in which the estimated standard deviations of the individual points are indicated by the short vertical lines. The curve for the γ-counts exhibits a bend at a sample thickness of about 1.5 g./cm.^{2}, which shows that the first part of this curve corresponds essentially to the relatively soft γ-rays (mostly internal-conversion K-series radiation), for which the mass absorption coefficient, μ/ρ, is known to be of the order of 0.7 cm.^{2}/g. in the diluting material used. The second, less steep, part of the curve naturally corresponds to the harder components of the nuclear γ-rays with $\mu/\rho \sim$ 0.1 cm.^{2}/g. in the diluting material, cf. Behounek.[1]

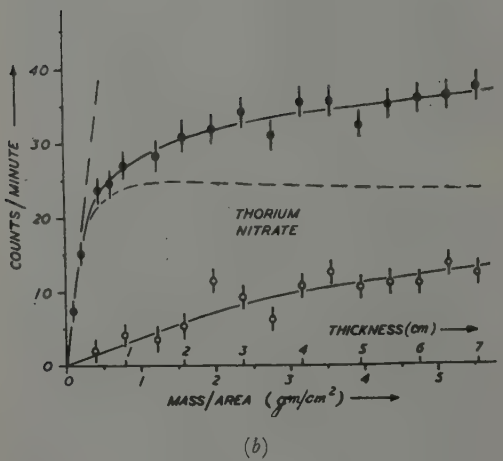
In Fig. 4(a), the broken curve for $n\beta$ is obtained by subtracting the γ- counts $n\gamma$ from the observed quantity $n\beta+n\gamma$, and the resulting curve is seen to start out almost linearly near the origin (*i.e.* for thin samples of less than 0.15 g./cm.^{2}) and to reach 70% of its saturation value at a thickness corresponding to 0.17 g./cm.^{2}. This linear region corresponds to approximate proportionality between the counting rate and the mass per unit area of the sample, so that the effect of absorption of the β rays is small in this region : thus at 0.17 g./cm.^{2} (corresponding to a thickness

TABLE 1.—β + γ AND γ COUNTING RATE FOR VARIOUS THICKNESSES OF 0.06% URANIUM (PITCHBLENDE) STANDARD.

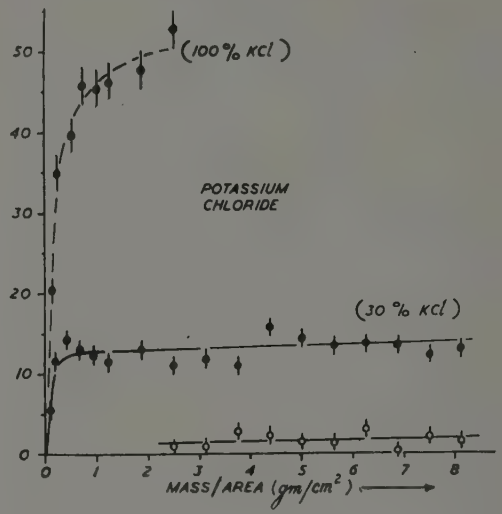
Approx. thickness (cm.) from microscope ..	0.20	0.40	0.60	0.80	1.00	1.50
Mass per unit area (g. sq. cm.)	0.095	0.216	0.347	0.476	0.627	0.891
Corrected thickness of sample (cm.)	0.16	0.36	0.57	0.79	1.03	1.47
$n\beta + n\gamma$ (counts/minute)	17.6	29.4	36.2	38.5	35.3	39.7
$n\gamma$ (counts/minute)	..	..	1.6	..	2.8	2.4



(a)



(b)



(c)

Fig. 4.—Experimental graphs showing total counting rate (solid circles), gamma counting rate (hollow circles) and beta counting rate (broken line) for the three standard samples (a) 0.06% uranium as pitchblende, (b) 0.5% thorium nitrate,(c) 30% potassium chloride, the broken line curve being for 100% KCl in this case.

of nearly 0.3 cm.) the curve falls only about 15% below the tangent at the origin. For larger thicknesses, the absorption is so great that the number of β counts becomes constant and no longer increases with sample thickness. All the important characteristics of the β and γ counts from pitchblende as deduced from the curves of Fig 4(a) are collected in the first row of Table 2, in which all the figures have been reduced to 0.1% uranium content, *i.e.*, 1 mg. uranium in 1 g. of sample. The last column gives the estimated γ counting rate for a thickness of 8 g./cm.,² which should yield about 80% of the saturation γ counts.

Figures 4(b) and 4(c) show the counting rate for the standard samples of 0.5% thorium nitrate and 30% potassium chloride, both being diluted with calcium carbonate. These curves exhibit the same general features as those of Fig. 4 (a) for pitchblende, and the relevant characteristic data obtained from them are also presented in Table 2. The curves for potassium are very near to those previously given by Hee, Wack and Jarovo [3] in their study of the β–radiation from rocks.

It is to be noted that if an exponential law is assumed for the absorption of the complex β-ray spectrum, then the figures in columns 4 and 5 of Table 2 should be equal. In actual fact, the two values are seen to be in the ratio of 1.30 ± 0.03, thus showing that such a law is not a good approximation. The lack of decay equilibrium of the thorium nitrate standard requires comment here. One of the decay products of thorium, *viz.*, radio-thorium (half life=1.9 years) is isotopic with thorium and is therefore to be found in the equilibrium proportion in chemically separated thorium compounds. All the decay products of radiothorium have short half-lives, the longest being 3.6 days for thorium X, so that these products will all be present in equilibrium with the radiothorium after a lapse of 10 days or so. The total activity of the thorium compound at any time can thus be estimated from the decay of

radiothorium and the formation of mesothorium 1 (half-life=0.7 years) and mesothoruim 2 (half-life=6 hours), which are products intermediate between radiothorium and thorium (half-life $=10^{10}$ years). The detailed estimates are given in Appendix I, and the conclusion is that the ratio, R, of the activity of a certain quantity of thorium as the chemical compound to that of the same quantity of thorium together with all its products in equilibrium is

$$R_\beta = 0.56 \pm 0.08 \quad \text{for the } \beta\text{-activity}$$

and $$R_\gamma = 0.65 \pm 0.06 \quad \text{for the } \gamma\text{-activity}$$

over the first 10 years. Since the age of the thorium nitrate used was known to be of the order of 3 to 7 years, the β and γ measurements made with it can be approximately corrected for lack of equilibrium by dividing by these factors, R_β and R_γ, respectively. The essential adequacy of this correction is confirmed by the fact that the corrected β-counts for thorium in equilibrium (columns 2 and 3 of Table 2) are found to be nearly two sevenths of the corresponding counts for pitchblende, *i.e.*, in the inverse ratio of the half-lives of thorium and uranium.

5. Analysis of Results

We can now analyze Table 2 to determine what quantitites to use for the most satisfactory discrimination between thorium and uranium. The four possible quantities are the following ratios : R_1 = (saturation β-counts /origin β + γ slope), R_2 = (origin γ slope/origin β + γ slope), R_3 = (γ slope at 4 g./cm.²/origin β + γ slope) and R_4=(γ counts at 8 g. per cm.²/saturation β counts). Values of these ratios for the measured standards are collected in Table 3 below, which shows that all of them do give a certain measure of discrimination. The third row of figures in Table 3 are the differences, $(R_{Th}-R_U)$, between corresponding ratios for thorium and uranium, together with the standard error of measurement of this difference with the apparatus previously described. Examination of these figures brings out the fact that the first ratio (R_1) will give very poor discrimination, and can be used at best as a confirmatory measurement. The other three ratios, all of which make a comparison between the γ and β counts, will give good discrimination, because the standard error of the measurement is one fifth to one tenth of the corresponding value of $(R_{Th}-R_U)$.

The best discrimination is given by R_3 but this requires accurate measurements of γ-counts for several sample thicknesses in the neighbourhood of 4 g./cm.². R_4 is second best, but has the great advantage that only two observations are required, one of the γ counts for a thickness of 8 g./cm.², and the other of the saturation β counts. R_2 ranks with R_4 in discriminating efficiency, but sufferes from the same drawback as R_3. It appears therefore that R_4 is the best discriminating ratio for the present purpose.

6. Estimation of the Uranium to Thorium Ratio

Since the measured value of any one of the above discriminating ratios, R_2, R_3, R_4, for a sample containing both uranium and thorium (in equilibrium with their decay products) will be intermediate between the values for uranium and thorium given in Table 3, it follows that either of these three ratios can be used to determine the relative proportions of uranium and thorium in the sample. The expected values of R_2, R_3 and R_4 for various ratios of uranium to (thorium + uranium) can be easily calculated by simple proportion using the data of Tables 2 and 3, and the results are shown in Table 4 and graphically in Fig. 5(a). All the graphs of this figure are

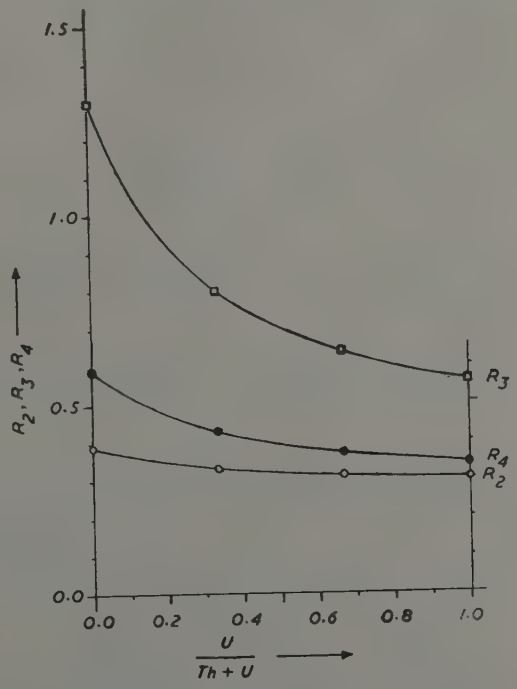


Fig. 5(a).—Graphs showing the values of the three best discriminating ratios, 10 R_2, 100 R_3, R_4, for different ratios of uranium/uranium + thorium).

TABLE 2.—SYNOPSIS OF MEASUREMENTS ON STANDARDS (REDUCED TO 1% OF ACTIVE SUBSTANCE).

Active substance	(β + γ) Counts				γ- Counts		
	Origin slope, counts per 1 g./cm.^{2}	Saturation β counts	Mass/area for 70% of saturation	Saturation β counts / Origin β slope	Origin slope, counts per 1 g./cm.^{2}	Slope at 4 g./cm.^{2}	Estimated** γ counts for a thickness of 8 g./cm.^{2}
Uranium (in pitchblende*) ..	280±10	62.4±1.0	0.17	0.23	8.3_3±0.2	1.58±0.15	21±1
Thorium (in thorium nitrate). ..	38±0.5	11.5±0.2	0.25	0.32	1.7_1±0.1	0.57±0.3	..
Thorium corrected to equilibrium ..	67.8	20.5	0.25	0.32	2.63	0.88	12±1
Potassium	(410±20)10^{-3}	(80±4)$\times 10^{-3}$	0.16	0.19_5	..	1×10^{-3}	$\sim 10\times10^{-3}$
Uranium (in uranyl nitrate) ..	184±5	64.3±0.9	0.26	0.35	0.4±0.2	0.4±0.2	..

* Some slight lack of equilibrium was suspected in the pitchblende sample, and it is possible that a correction of about 10% may be required for the experimental values.

** The estimate is a valid extrapolation because the value of μ/ρ is less than 0.1 for the harder group.

TABLE 3.—COMPARATIVE STUDY OF THE POSSIBLE DISCRIMINATING RATIOS.

Active substance	R_1 = Saturation β counts / Origin (β+γ) slope	R_2 = Origin γ slope / Origin (β + γ) slope	R_3 = γ slope at 4g./cm^2 / 3 Origin (β + γ) slope	R_4 = γcounts at 8 g./cm^2 / Saturationβ counts
Thorium (corrected)	0.30±0.01	(0.39±0.02)$\times 10^{-1}$	(1.30±0.04)$\times 10^{-2}$	0.59±0.05
Uranium	0.22±0.01	(0.30±0.01)$\times 10^{-1}$	(0.56±0.02)$\times 10^{-2}$	0.34±0.02
RTh—RU	0.08±0.02	(0.09±0.02)$\times 10^{-1}$	(0.74±0.04)$\times 10^{-2}$	0.25±0.05
Potassium	0.195±0.01	0.02×10^{-1}	(0.24±0.05)$\times 10^{-2}$	0.1
Uranium in uranyl nitrate	0.35±0.01	(0.02±0.01)$\times 10^{-1}$	(0.22±0.1)$\times 10^{-2}$	..

TABLE 4.—COMPARISON OF VARIOUS DISCRIMINATING RATIOS FOR THE QUANTITATIVE ESTIMATION OF URANIUM/(THORIUM + URANIUM).

Th : U	U / Th+U	R_2 = Origin γ slope / Origin (β+γ) slope	R_3 = slope at 4g./cm. / Origin (β + γ) slope	R_4 = 8g./cm. γ counts / Saturation β counts	0.01 / R_2	0.01 / R_3	1 / R_4
3: 0	0.00	(0.39±0.02)$\times 10^{-1}$	(1.30±0.04)$\times 10^{-2}$	0.59±0.05	2.56±0.1	0.77±0.02	1.71±0.1
2: 1	0.33	0.33×10^{-1}	0.80×10^{-2}	0.43	3.06	1.25	2.30
1: 2	0.67	0.31×10^{-1}	0.64×10^{-2}	0.37	3.25	1.55	2.69
0: 3	1.00	(0.30±0.01)$\times 10^{-1}$	(0.56±0.02)$\times 10^{-2}$	0.34±0.02	3.36±0.1	1.77±0.05	2.97±0.2

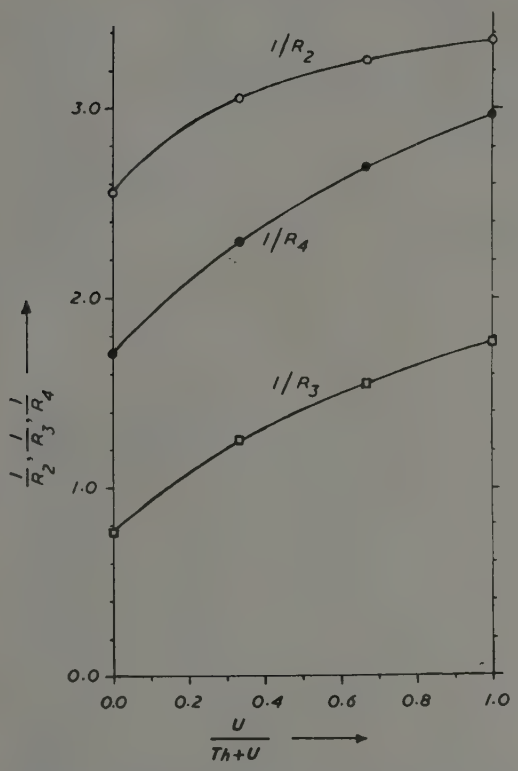


Fig. 5(b).—The corresponding graphs for the reciprocals of these ratios, viz. $0.1/R_2$, $0.01/R_3$ and $1/R_4$, showing the improved character of the curves.

seen to be strongly curved, especially that for R_3, and are therefore rather unsuitable for quantitative work. This defect can be easily remedied in the case of R_3 and R_4 by plotting $0.01/R_3$ and $1/R_4$ against relative percentage of uranium to (thorium+uranium), which gives the much improved graphs shown in Fig. 5(b). Combining this with the considerations of the previous section, we find that $1/R_4$ is the best discriminating ratio. If we assume an accuracy of 5% in the γ-counting rate, which is readily attained, we get a margin of about 0.1 in the measured value of $1/R_4$. It follows from Fig. 5(b) that we can determine the relative proportion of uranium and thorium to within 5% with this type of measurement. The design and testing of a discriminator based on the foregoing analysis will be described in a later communication, while Appendix II gives an example of the application of the detailed analysis along the patterns of Fig. 4.

As regards the influence of potassium on the counting rates, it is enough to note that both the β and γ counts for potassium are about 1/1000 of those obtained with corresponding quantities of uranium. Thus 10% of potassium in the sample will be equivalent to about 0.01% of uranium, and its presence will not therefore produce significant error unless the (uranium + thorium) content of the sample is as low as 0.1%. For such extremely poor ores, a correction for the activity of potassium can be readily applied using the data of Table 2, provided the potassium content is known approximately from a chemical determination.

Acknowledgements

The authors are grateful to Dr. Nazir Ahmad, Chairman, Atomic Energy Commission, for his interest in the work, and to Mr. Abdul Hai for carrying out some of the chemical analyses.

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Appendix I

Estimate of the Activity of Thorium Nitrate Preparation

(a) Members of the thorium series isotopic with thorium and therefore initially present are : (1) thorium (half-life=10^{10} years) and (2) radiothorium (half-life=1.9 years).

(b) The intermediate products are mesothorium 1 (half-life=6.7 years) followed by mesothorium 2 (half-life=6.1 hours).

(c) All the other products, *i.e.*, those after radiothorium have short half-lives with a maximum of 3.6 days for thorium X.

Thus the activity A (t) at any time t ($>>3.6$ days) can be represented by

$$A(t) = A_{Th} + (A_{Mes1} + A_{Mes2}) + (A_{Radth} + A(\text{of decay products}))$$
$$= A_{Th} + \text{Constant} \times A_{Mes1} + \text{Constant} \times A_{Radth}.$$

Since thorium itself is only α-active, the problem reduces to estimating the relative activites of radiothorium and mesothorium 1, with which mesothorium 2 will be in equilibrium after a period exceeding a day. Let the number

of atoms of thorium disintegrating per second be N_0. Then

$A_{Mes_I} = N_I$ = number of atoms of mesothorium disintegrating per second.

$$= N_0 (1\text{-exp } [-\lambda_I t])$$

where $\lambda_I = 0.693/6{,}7$ year^{-1},

and $A_{Radth} = N_2$ = number of atoms of radiothorium disintegrating per second.

$$= N_0 \text{ exp } [-\lambda_2 t] + N_0 (1 - \text{exp } [-\lambda_I t])$$

$$= N_0 (1 - \text{exp } [-\lambda_I t] (1 - \text{exp } [(-\lambda_2 - \lambda_I)t])).$$

Table 5 gives the values of N_I/N_0 and N_2/N_0 for various values of time elapsed since the separation of the thorium. Now there are two β-emitters among radiothorium and its equilibrium products, and two among mesothorium and its products. On the assumption of similar spectra for these four emitters, the β-activity of the thorium should be proportional to

$$\frac{1}{4}\left(2\frac{N_I}{N_0} + 2\frac{N_2}{N_0}\right) = \frac{1}{2}\left(\frac{N_I}{N_0} + \frac{N_2}{N_0}\right).$$

By a similar reasoning, the γ-activity should be proportional to

$$\left(\frac{3}{4}\frac{N_I}{N_0} + \frac{1}{4}\frac{N_2}{N_0}\right).$$

These two ratios are tabulated in the third and fourth rows of the table under the labels of relative β activity and relative γ activity, respectively. They are both seen to fall rapidly and reach a minimum after about 2 years, and then to increase slowly towards unity during the next 20 years. The average values of these ratios obtained graphically over the first ten years are given in the last column of the table and they can be used as correction factors for a thorium compound, whose age lies within this period. The corresponding factors for the next ten year period are closer to unity, being both very nearly 0.85± 0.09.

Appendix II

Direct Application to an Unknown Sample

A direct application of the data of Fig. 4 can be made to an unknown mineral, albeit with the expenditure of considerable time and trouble. The (β + γ) and γ counting rates for different quantities upto 6 g./cm.^{2} of an unknown sample are plotted in Fig. 6, in which the broken line shows the β counting rate obtained by subtracting one curve from the other. The graphs are seen to be very different from those for pitchblende, but closely resemble those for thorium, thus suggesting that thorium is the major radioactive constituent of the sample. An evaluation of the ratios $0.01/R_3$ and $1/R_4$ gives 0.61 ± 0.02 and 1.31 ± 0.1, respectively, both of which are close to the corresponding values for thorium, but lie well outside the range for thorium-uranium mixtures (Table 4 and Fig. 5). Thus there would appear to be no possibility of the presence of any uranium in the sample.

TABLE 5

Time (years)	0	1	2	4	6	8	10	15	20	Mean for first 10 years
N_I/N_0	1.000	0.834	0.714	0.643	0.659	0.706	0.759	0.866	0.930	
N_2/N_0	0.000	0.120	0.232	0.410	0.547	0.652	0.733	0.862	0.929	
Estimated relative β—activity	0.500	0.477	0.473	0.526	0.603	0.679	0.746	0.864	0.930	$0.56_5 \pm 0.08$
Estimated relative γ-activity	0.750	0.655	0.594	0.585	0.631	0.692	0.752	0.865	0.930	$0.65_2 \pm 0.06$
Relative (γ/β) .. .. ratio	1.50	1.37	1.26	1.11	1.05	1.02	1.01	1.00	1.00	1.15±0.2

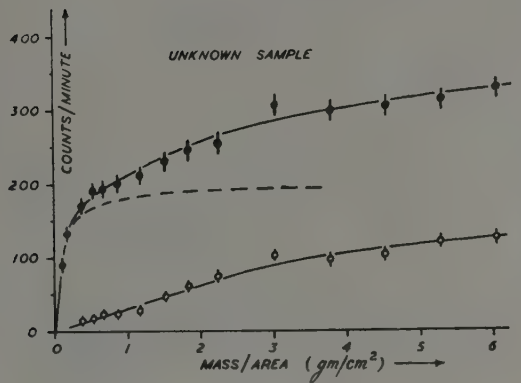


Fig. 6.—The gamma, beta, and total counting rates for various thicknesses of an unknown sample. Total rate, solid circles; gamms rate, hollow circles; beta rate, broken line.

Assuming first that all the activity is due to thorium, we get from the measured β and γ counting rates the following estimates of thorium content :

β Counting gives .. 1.1₀±0.1 %
γ Counting gives .. 1.4₀±0.1 %

The discrepancy between the two estimates points to the presence of some other constituent, which has a higher γ/β emission ratio than thorium. This idea was confirmed by the chemical analysis of the sample, which gave a thorium content of only 0.6±0.05%. This would account for a trifle more than half the β-counts and less than half of the γ-counts. The counts remaining unaccounted for are tabulated below :

Origin β+γ slope	Saturation β counts	Origin γ slope	γ slope at 4 g./cm.²	γ counts at 8 g./cm.²
400	70	16	9	70

Such a distribution of β and γ counts could be due to the decay products of uranium that have been separated from the parent material by weathering action. These decay products are known to be strongly γ-active, cf. for instance the various counting rates for uranium in pitchblende and in uranyl acetate given in Table 2. On this basis, the above residual activity would correspond to an original uranium content of about 0.4%.

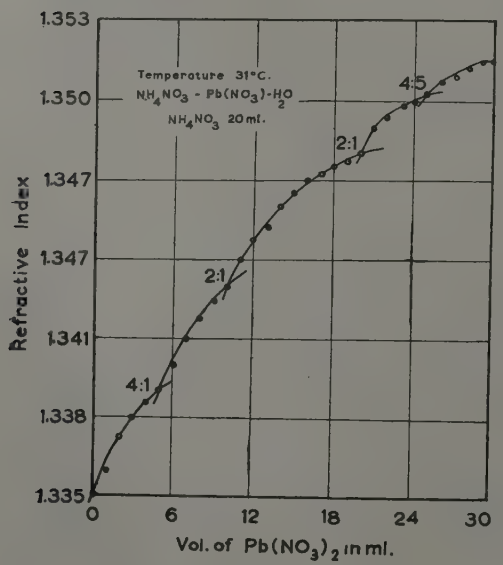
REFRACTOMETRIC STUDIES OF COMPLEX SALT FORMATION

M. A. Azim and Mazhar-ul-Haque

Chemistry Department, Government College, Lahore

Complex salt formation has been studied by various workers by determination of magnetic susceptibility,[1] which showed an abnormal behaviour in case of formation of complex salts. Other physical properties, like surface tension, viscosity and refractive index, have also been found to give an indication as to the formation of double and complex salts.[2] Since different properties may respond to differant types, therefore we tried to investigate the variation of refractive index for cases in which complex salt formation was noticed by magnetic susceptibility determination. The principle of the refractometric method depends upon the fact that when a certain volume of solution of one substance is added to a definite volume of the solution of another substance at the given temperature, the refractive index goes on increasing or decreasing gradually; but at a certain point the increase or decrease is abnormal. When a graph is plotted between the refractive index and the volume of the solution added, a kink in the curve is noticed at the point where complex salt formation takes place. Several systems were examined by this method, and the present communication deals with the results for:

(1) NH_4NO_3—$Pb(NO_3)_2$-H_2O



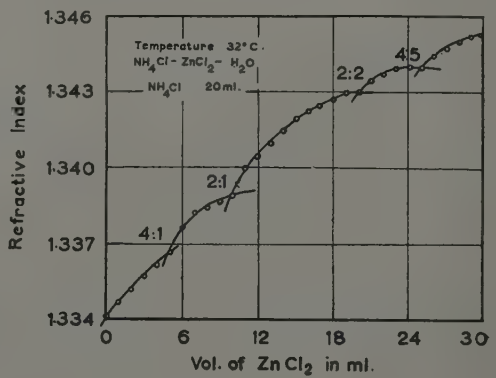
(2) NH_4Cl—$Zn\,Cl_2$-H_2O
(3) NH_4Cl—$Cd\,Cl_2$-H_2O
(4) NH_4OH-$Cu\,SO_4$—$Cu(OH)_2.(NH_3)_2$ or $Cu(OH)_2.(NH_3)_4$
(5) $CHCl_3$—$C_2H_5OC_2H_5$ (ether)
(6) $CHCl_3$—$(CH_3)_2.CO$

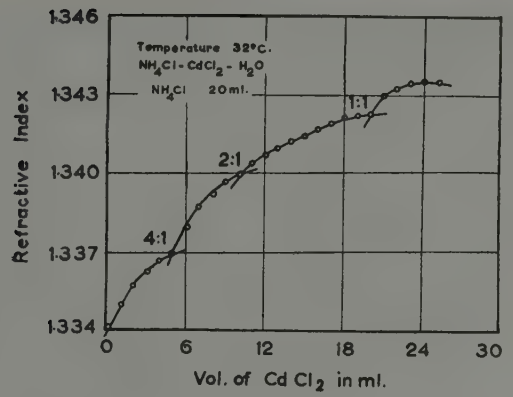
The following systems were also examined, but we failed to get any indication of double salt or complex salt formation due to precipitate formation:

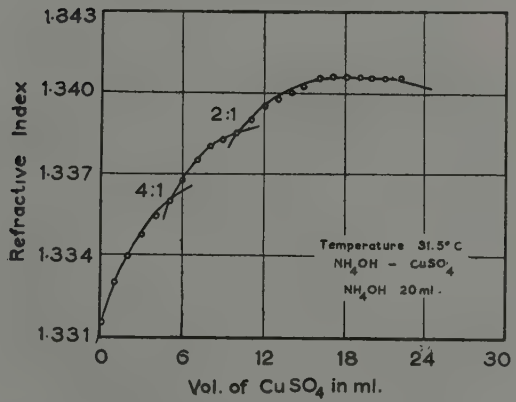
(1) *p*-Toluidine—*p*-chlorophenol
(2) *p*-Toluidine—*o*-chlorophenol
(3) $Ni(SO_4)$—$(NH_4)_2.SO_4$
(4) KCN—$AgNO_3$
(5) NaOH—Na_2SO_4
(6) $K_4Fe(CN)_6$—$FeCl_3$

Experimental

Thirty mixtures of each system were made up by adding varying amount (0-30 cc.) of molar solution of one of the components to 20 cc. or 10 cc. of molar solution of another, and the mixture was diluted to 50 cc. in each case. The refractive indices of these mixtures were determined at constant temperature with a critical angle refractometer (Bellingham & Stanley Ltd.) with an accuracy of $\pm$ 0.0002. The temperature of the solution under investigation was controlled within $\pm$ 0.1°. A graph was plotted between the refractive index and the volume of the varying component. Kinks in the curve were obtained at those points where the complex or the double salt formation took place.







From the position of kinks in the curves molar ratios of the components of the double and complex salts were calculated and are detailed below:

(1) NH_4NO_3—Pb $(NO_3)_2$-H_2O 4:1, 2:1, 1:1, 4:5

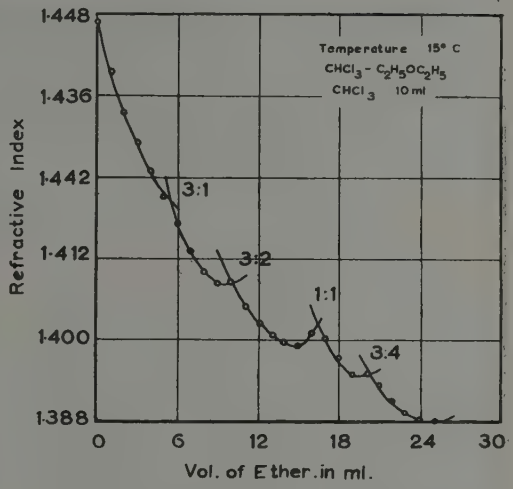
All the first three values, 4:1, 2:1 and 1:1, confirm the results obtained by magnetic susceptibility method but the fourth value, *i.e.*, 4:5, is another ratio found by refractometric method which is probably more sensitive than magnetic method.

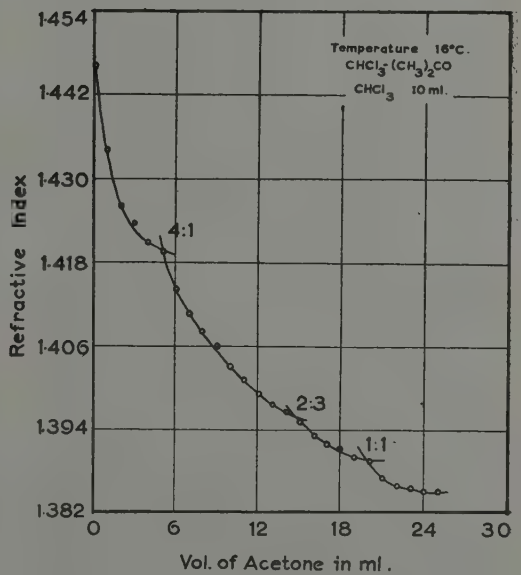
(2) NH_4Cl—Zn Cl_2-H_2O 4:1, 2:1, 1:1, 4:5

In this case also 4:1, 2:1 and 1:1 values are in agreement with the magnetic susceptibility method but the value 4:5 is another ratio found only by this method.

(3) NH_4Cl—Cd Cl_2-H_2O 4:1, 2:1, 1:1

4:1-1:1 are the values which are obtained by by the magnetic susceptibility method. While 2:1 value obtained by our method is a new value.





(4) NH_4OH-Cu SO_4—Cu$(OH)_2$.(NH_3) 4:1, 2:1 or Cu$(OH)_2$-$(NH_3)_4$ Schweitzer's reagent

(5) CH Cl_3—C_2H_5O C_2H_5 2:1, 1:1, 5:8 and 1:2

(6) $CHCl_3$—$(CH_3)_2CO$ 2:1, 2:3 and 1:2

The values obtained in systems 4 to 6 have not been determined before by any method.

References

1. Prasad and Datar, Proc. Indian Acad. Sci., **36A**, 544 (1952).
2. C.S. Pande and M.P. Bhatnagar, J. Indian Chem. Soc., **31**, 402 (1945).

STUDIES IN THE INFLUENCE OF LONG CHAIN PHENOLIC ADDITIVES ON THE VISCOSITY OF MINERAL OILS

Part III.—Measurement and Analysis of the Viscosity Depression Occurring in Mixtures of Mineral Oils with (A) Allylphenol, (B) Allylbenzene and (C) Allylcatechol *

ZIA-UR-RAHMAN, MAZHAR MAHMOOD QURASHI AND GEORGE HAHN

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

1. Introduction

In previous communications of this series,[1,2] an analysis was given for the viscosity depression produced in mineral oils by the additions of various proportions of bhilawan shell liquid, bhilawanol, and its methylation products. It has been previously suggested by various workers[3] that the viscosity depression is attributable to the varying degrees of association of the phenolic component, and this is supported by the fact that the absolute magnitude of the viscosity depresion decreases as the number of phenolic OH groups per molecule decreases, from two in bhilawanol to zero in dimethoxybhilawanol.[2] However, an anomaly presented itself in the cases of (a) bhilawan shell liquid, which exhibits a much larger viscosity depression than bhilawanol, whereas its constituents do not contain more than two hydroxyls per molecule, and (b) dimethoxybhilawanol, which has no free hydroxyl group, but still shows a marked viscosity depression. This led to a consideration of the relation between the viscosity, ν, of the product and the viscosity depression, $\Delta\nu$, produced on mixing it with a mineral oil of the same viscosity. The ultimate conclusion was that this depression is very nearly proportional to the quantity $\nu^{1.33}$ over the whole 75-fold range of viscosities studied, and that it does not show any other direct correlation with the number of free hydroxyl groups in the compounds, whence it was deduced that the function $\Delta\psi_{0.33}=\Delta(\nu^{-0.33}-1)/0.33$ is the same for all these compounds.

Especially significant is the fact that this function $\Delta\psi$ does not become zero suddenly on methylation of both the hydroxyl groups, thus suggesting that ψ measures perhaps a more fundamental property of the liquids. In order to investigate these suggestions further, it was decided to study synthetic phenolic and benzene compounds with short side chains, both saturated and unsaturated. The present communication deals with the results obtained with allylphenol, allylbenzene and allylcatechol, all of which have the benzene nucleus with a C_3H_5 allyl side chain.

2. Preparation of Compounds

(*a*) *Allylphenol.*—A mixture of 188 g. of phenol, 242 g. of allyl bromide, 280 g. of finely powdered calcined potassium carbonate and 300 g. of pure dry acetone was refluxed on a steam bath for eight hours. A heavy precipitate of potassium bromide began to form soon after the refluxing started. After cooling, water was added to the reaction mixture, and the product was taken up in ether and washed twice with 10% sodium hydroxide solution. The ethereal solution was dried over potassium carbonate and, after removal of the ether, the residue was distilled under reduced pressure. This gave about 150 g. of allyl phenyl ether, boiling at 85 °C./ 19 mm. of Hg. This is converted into the allyl phenol by the Claisen rearrangement, in which the allyl group migrates only to the ortho position.

The allyl phenyl ether was boiled in a flask with a reflux tube for about 2½ hours, when the rearrangement was substantially complete. The product was dissolved in 20% sodium carbonate solution, the solution was acidified, and the phenol extracted with ether. The extract was dried over calcium chloride and then distilled under reduced pressure. About 90 g. of allylphenol boiling at 103° to 105 °C.. under a pressure of 19 mm. of Hg were obtained. (Standard data are : b.p., 99 °C./12 mm. and 220 °C./ 760 mm. of Hg; $n_D^{20}=1.5453$). The completion of the rearrangement was confirmed by preparing a derivative, *viz.*, 2-methyl-dihydrobenzofuran, by reaction in acetic acid with 45% aqueous hydrobromic acid, followed by refluxing for twenty minutes, addition of excess water and extraction with ether. The ethereal extract was washed with sodium hydroxide, dried, and distilled to give a 50% yield of material boiling at 86° to 88 °C./19 mm. of Hg, a tarry residue being left behind. The viscosity of the allylphenol at 40 °C. was found to be 3.107 centistokes.

* The present communication is based in part on a thesis submitted by Zia-ur-Rahman for the M.Sc. degree to the University of Karachi.

(*b*) *Allylbenzene.*—By reacting 20 g. of magnesium shavings with a mixture of 78.5 g. of pure bromobenzene and 350 ml. of dry ether dropped gradually from a dropping funnel, Grignard reagent was prepared. Through the dropping funnel, 57.5 g. of allyl bromide were added dropwise to the Grignard reagent, and the reaction was completed by heating for half an hour. After adding 100 ml. of water and cooling the flask in ice-cold water, the ethereal layer containing the allylbenzene was separated in a separating funnel, washed with a little water and then dried over calcium chloride. After removal of the ether, the product was distilled in an air bath, the fraction distilling over between 150—160 °C./760 mm. of Hg. being collected. By redistillation, the pure substance boiling at 155—158 °C. was obtained.

(*c*) *Allylcatechol.*—132 g. of catechol and 144 g. of pure allyl bromide were dissolved in 220 ml. of pure dry acetone. Finely divided powdered potassium carbonate (freshly heated to remove moisture) was added gradually with constant shaking, and the mixture was refluxed for 7 hours on a water bath, a calcium chloride tube being attached to the condenser. After removal of the acetone and addition of dilute sulphuric acid, the mixture was extracted with ether. By washing with dilute alkali, the monoallyl ether and the unreacted catechol were removed, the ethereal solution being dried and evaporated to give 30 g. of the diallyl ether. The alkali washings were immediately acidified and the oil taken up in chloroform. The catechol having been removed by repeatedly washing with water, the chloroform was evaporated off, and the oil remaining behind was distilled under reduced pressure to give 60 g. of pure mono-allyl ether.

The molecular rearrangement of the mono-allyl ether was carried out by heating it in a flask fitted with a condenser to 170—180 °C. in a paraffin bath. The inner temperature rose suddenly to 225 °C. with momentary boiling, the colour of the liquid changing to red. After cooling, the product was fractionated under a pressure of 16 mm. of Hg and the fraction boiling at 142 °—159 °C./16 mm. was collected. The yield was about 25 g. The viscosity of the compound measured at 40 °C. was found to be 13.9 c.s. Some more of the compound was prepared and its viscosity was found to be 18.2 c.s. *i.e.* about 4 c.s. higher than the visocsity of the previous lot. Both were redistilled, after which concordant viscosity measurements were obtained, *viz.* 18.5_8 c.s. for the first lot and 18.5_2 for the second lot.

3. Measurements with Allylphenol

The viscosity of the allylphenol awas measured with U-tube viscometer No. 1 of the B.S.S. pattern, supported vertically in a water bath, whose temperature was maintained at 40.0° ± 0.1 °C. Drying tubes were connected to the two limbs of the viscometer to prevent the entry of moisture, and the mean of several readings of the time of flow was taken. The mean value obtained for the kinematic viscosity at 40 °C. was 3.10_7 c.s.

A straight mineral oil (B.O.C. "H.S.D.") of nearly the same viscosity was selected, and its viscosity was also measured at 40 °C. with the above-mentioned viscometer and was found to be 3.18_2 c.s. This was considered close enough to the viscosity of allylphenol for carrying out measurements of viscosity depression produced on mixing. Allylphenol was mixed in various proportions with the mineral oil and the kinematic viscosity of each mixture was measured at the fixed temperature of 40 °C. The compositions of the various mixtures were selected in such a way as to obtain a uniform distribution of experimental points over the whole length of the curve. The viscosities of the pure allylphenol and the mineral oil were again measured at the end, and were found to be 3.09_2 and 3.19_8 c.s., respectively. The experimental results are given in Table 1.

A small correction is required for the difference of 0.090 c.s. in viscosity between the allylphenol and the oil. As discussed in a previous paper,[2] this correction can, to a sufficient approximation, be applied by assuming the variation

TABLE 1.—VISCOSITY AT 40 °C. OF MIXTURES OF ALLYLPHENOL WITH B.O.C. "H.S.D." OIL.

Wt% allylphenol=100 × x	0.0	9.5	18.2	28.5	39.0	50.2	59.3	70.6	81.2	90.8	100.0
Measured viscosity (centistokes)	3.19_0	2.97_3	2.87_2	2.82_4	2.817	2.81_4	2.81_8	2.84_0	2.89_0	2.96_4	3.10_0
Viscosity for ideal solution (centistokes)	3.19_0	3.180	3.17_4	3.164	3.155	3.145	3.137	3.126	3.117	3.10_8	3.10_0
—Δv=viscosity depression (centistokes)	0.000	0.207	0.30_2	0.340	0.338	0.331	0.319	0.286	0.227	0.14_4	0.000

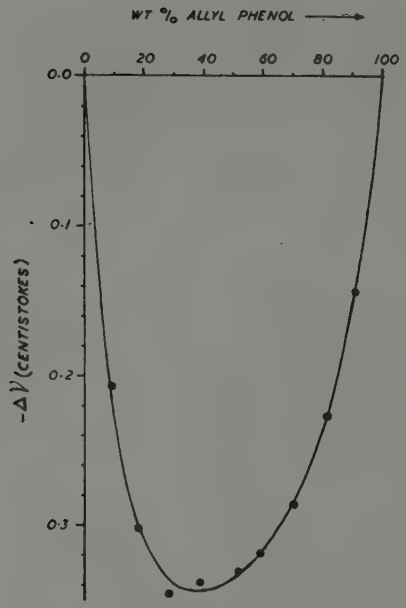


Fig. 1.—Graph showing the viscosity depression, $-\Delta\nu$, observed in mixtures of allylphenol with mineral oil (B.O.C. "H.S.D": ν=3.19 c.s.)

of the viscosity for ideal solution to be linear with composition by weight. The values of the depression, $-\Delta\nu$, obtained are given in the last row of Table 1, and the corresponding graph is seen in Fig. 1. The values of $-(\partial\nu/\partial x)_{x=0}$ where x are the parts by weight of allylphenol, and $(-\Delta\nu_m)$ the maximum depression are obtained from the graph as 2.85 c.s./part and 0.344 c.s., respectively.

It will be noted that the viscosity of the mineral oil used above is about 3% higher than that of the allylphenol. It was therefore thought desirable to repeat the above measurements using an oil with a viscosity lower than that of the allylphenol. Such an oil was prepared by blending the "H.S.D." oil with 1/7 by volume of

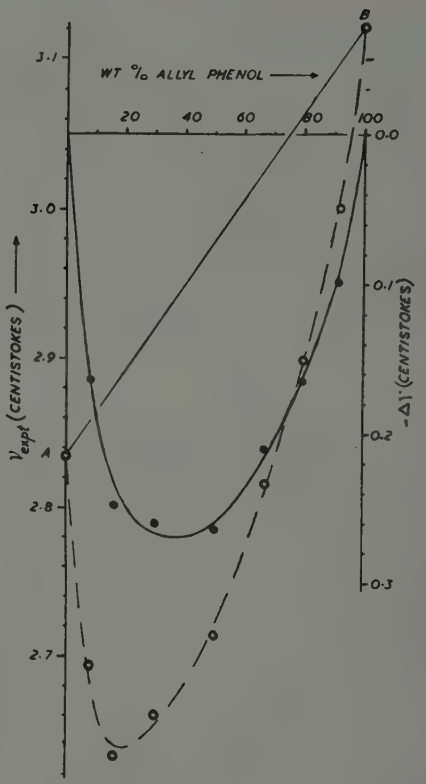


Fig. 2.—Graphs showing the measured viscosities, νexpt, and the calculated viscosity depression for mixtures of allylphenol with a mineral oil blend (ν=2.835 c.s.). νexpt : hollow circles and broken line graph. $-\Delta\nu$: solid circles and full line graph.

kerosene oil having a viscosity of 1.15 centistokes, and the blend was found to have a viscosity of 2.84 centistokes. The measurements for the mixtures with allylphenol at 40°C. (corrected for changing viscosity* of the blended oil) are given in Table 2, and are plotted inFig 2 (broken line).

*It was found that the viscosity of the mineral oil blend increased slowly during the course of the experiment, probably due to loss of the more volatile kerosene oil.

TABLE 2.—VISCOSITY AT 40°C. OF MIXTURES OF ALLYLPHENOL WITH MINERAL OIL BLEND.

Wt.% allylphenol=100x	0.0	8.0	16.0	30.1	50.3	67.0	80.0	92.0	100.0
Measured viscosity (centistokes)	2.835	2.694	2.633	2.661	2.715	2.817	2.900	3.001	3.122
Calculated viscosity for ideal solution (centistokes)	2.835	2.858	2.881	2.921	2.979	3.027	3.065	3.099	3.122
Depression $-\Delta\nu$	0.000	0.164	0.248	0.260	0.264	0.210	0.165	0.098	.000

The slightly higher value for the viscosity of the allylphenol in this second set of experiments may be due to partial oxidation as in the case of bhilawanol.[1] The values of viscosity of the various compositions on the basis of ideal solution are given as before by the straight line AB, and are to be found in the third row of Table 2, while the deduced viscosity depression, $-\Delta\nu$, is given in the fourth row of the table. The graph for $\Delta\nu$ is ploted in Fig. 2 (full line), and from it we obtain $-(\partial\nu/\partial x)_{x=0} = 2.40$ c.s./part $(-\Delta\nu_m) = 0.26_8$ c.s., which are both lower than the previous values by about 20%. This is quite satisfactory when we remember that in Fig. 2 the correction for the difference of viscosity between the two components of the mixture is about 0.1 centistokes as against the corrected value of 0.26_8 c.s. for $-\Delta\nu_m$. In fact, the degree of agreement between the two sets of values (from Figs. 1 and 2) affords confirmation of the essential validity of the corrections. The means of the two values are:— $[-(\partial\nu/\partial x)_{x=0}] = 2.6_2 \pm 0.22$ c.s./part and $-\Delta\nu_m = 0.30_6 \pm 0.038$ c.s.

It is to be noted here that when the more accurate procedure is adopted and ν ideal is taken to vary linearly with mole fraction (instead of weight%), the mean values obtained above remain unchanged, but the standard errors are reduced to two-thirds.

4. Measurements with Allylbenzene

The measurements for allylbenzene were also made by mixing it with two different oil blends, namely, (1) kerosene oil and *n*-heptane, and (2) kerosene oil and petroleum ether. The viscosities were measured with a semi-micro viscometer of 1.5 ml. capacity, which had previously been calibrated with distilled water at several temperatures from 40°C. to 70°C., giving the following values of the constants

$$A = 0.009{,}52$$

$$B/50^2 < 0.000{,}05$$

Allylbenzene was found to have a viscosity of 0.724 c.s. at 40°C., and a blend of kerosene oil ($\nu = 1.15$ c.s.) with *n*-heptane ($\nu = 0.33$ c.s.) in the ratio of 2:3 had a viscosity of 0.728 c.s. measured at 40°C. in the same viscometer. Allylbenzene was mixed in various proportions (increasing by steps of 10%) with this blended oil, with gentle shaking in a stoppered bottle to avoid loss of the volatile heptane. As a further precaution against such a loss during the experiment, a fresh mixture was prepared for each concentration of allylbenzene in place of the more economical method of adding more allylbenzene to the mixture used for the lower concentration. At least three measurements of the time of flow concordant to 1/2% were taken for each concentration, and their mean was used to calculate the viscosity as $\nu = At$, the kinetic energy term, B/t^2, being negligible with the viscometer used here. The viscosities of allylbenzene and the oil blend were measured at the end of the experiment and the overall mean values were used. The measured viscosites are given in Table 3, and are plotted against wt.% allylbenzene in Fig. 3 (hollow circles, broken line). A satisfactorily smooth curve can be drawn through the points, the standard deviation of the points from this curve being nearly 0.003 c.s., which corresponds to 0.4% of the mean viscosity (0.70 c.s.). This compares satisfactorily with the experimental accuracy of each viscosity measurement which is of the order of 1/4%. As before, the line $A_I B_I$ represents the viscosity of ideal mixtures of allylbenzene with the blended oil, and both $-(\partial\nu/\partial x)_{x=0}$ and $-\Delta\nu_m$ can be reckoned from this line as reference, giving

$$-(\partial\nu/\partial x)_{x=0} = 0.22 \pm 0.05 \quad \text{and}$$

$$-\Delta\nu_m = 0.039_5 \pm 0.004.$$

The whole series of observations was repeated with another oil blend of viscosity 0.727 c.s. made

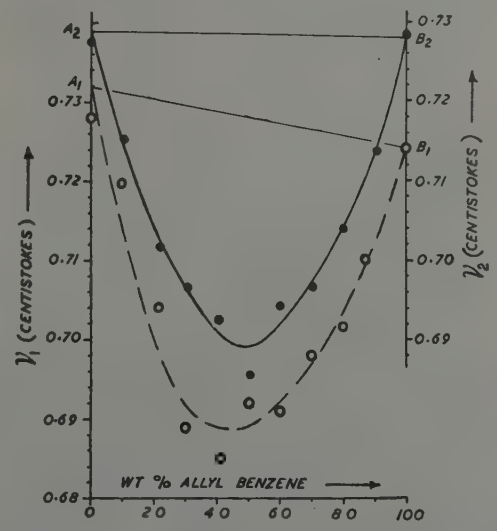


Fig. 3.—Graphs for viscosity depression, $-\Delta\nu$, observed in mixtures of allylbenzene with (a) blend of kerosene oil and *n*-heptane, shown by the broken line, and (b) blend of kerosene oil and petroleum ether, shown by the full line curve.

TABLE 3.—VISCOSITY AT 40°C. OF MIXTURES OF ALLYLBENZENE WITH TWO MINERAL OIL BLENDS.

Mixtures with the oil-heptane blend	100 x = Wt. % allylbenzene	0	10.0	21.4	30.1	41.3	49.9	59.8	70.0	80.1	87.0	100
	Viscosity	0.728	0.719_5	0.704	0.698	0.685	0.692	0.691	0.698	0.701_5	0.710	0.724
Mixtures with the oil-petrolether blend	100 x = Wt. % allylbenzene	0	10.3	21.2	30.2	40.1	50.4	60.0	70.0	80.0	90.3	100
	Viscosity	0.727_5	0.715	0.701_5	0.696_5	0.692_5	0.685_5	0.694	0.6965	0.704	0.713_5	0.728_5

from the kerosene oil and pertoleum ether (*i.e.* low-boiling petroleum fraction, b.p. 60—80°C. $\nu_{40}=0.44$ c.s.) in the ratio of 3:2. The measured viscosities of mixtures of this blend with allylbenzene are given in the lower half of Table 3, and are shown graphically in Fig. 3, full line curve. The standard deviation of the points about this curve is 0.002 c.s., *i.e.* 2/3 of that with the previous blend, and the graph yields

$$-(\partial\nu/\partial x)_{x=0}=0.15\pm0.03 \text{ and}$$
$$-\Delta\nu_m = 0.0394\pm0.003.$$

This gives the following overall mean values :

$$\text{Mean } -(\partial\nu/\partial x)_{x=0} = 0.18_5 \pm 0.03_5 \text{ and}$$
$$\text{mean } -\Delta\nu_m = 0.0394 \pm 0.002_5.$$

It is to be noted that the viscosity of allylbenzene in the second graph is apparently about 0.6% higher than in the first, which may be attributed largely to experimental error.

5. Experiments with Allylcatechol

(*a*) *Determination of the Miscibility Curve.*—It was suspected that allylcatechol might not be as readily miscible with mineral oils as are allylphenol and allylbenzene, and indeed a well shaken mixture of 10% allylphenol with 90% of mineral oil of viscosity 19 centistokes at 40°C. (blend of B.O.C. " 50 " and " H.S.D. " in the ratio of 10:1) was found to separate into two distinct layers at room temperature (nearly 30°C.). However, on heating to 80°C., the allylcatechol dissolved completely in the oil. It was therefore thought necessary to determine the miscibility curve for the two liquids in order that the viscosity measurements could be made in the region of complete miscibility. Mixtures of the allylcatechol and the oil in various proportions were taken in test tubes, and were slowly heated (with constant stirring) in a water bath, and the temperature at which the turbidity disappeared was noted for each mixture. The bath was allowed to cool, and the temperature at which turbidity re-appeared was noted, the mean of the two temperatures being taken as the miscibility temperature for the particular mixture. The results are given in Table 4, and the miscibility curve is drawn in Fig. 4. The standard deviation of the points about the curve is less than 2°C., which agrees well with that estimated from the measurements in Table 4. It follows from an inspection of Fig. 4 that we must work at a temperature of over 125°C. in order to obtain a reliable value for $-\Delta\nu_m$, which can then be extrapolated to 40°C., if we at the same time determine experimentally the temperature variation of the viscosity depression. For obtaining $-(\partial\nu/\partial x)_{x=0}$ we require measurements in the range 0—15% allylcatechol, and therefore we need not go much above 90°C.

(*b*) *Viscosity Measurements.*—For these measurements, a B.S.S. pattern U-tube viscometer No. 2 was used, which has the advantage of a wide capillary, thus lessening the danger of clogging errors caused by possible decomposition at the elevated temperatures necessary for the present measurements. The times of flow are also small, of the order of 1 minute, which necessitates use of the kinetic energy correction, but

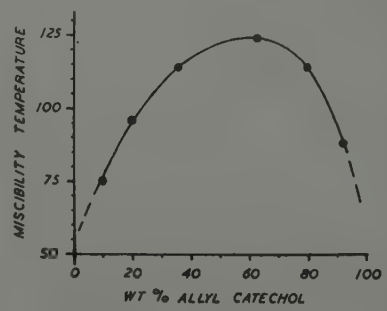


Fig. 4.—Miscibility curve for mixtures of allylcatechol with mineral oil of viscosity 19 centistokes at (40°C.), showing that the critical solution temperature is 125°C.

TABLE 4.—MISCIBILITY TEMPERATURES OF MIXTURES OF ALLYLCATECHOL WITH MINERAL OIL.

Wt.% allylcatechol	9.8	19.6	35.5	62.5	79.8	91.9
Turbidity disappears at (°C.)	88	106	120	125	115	90
Turbidity appears at (°C.)	62	86	109	124	112	86
Mean miscibility temperature (°C)	75	96	114	124	114	88

provides a compensating advantage in that the time for which the mixtures are to be heated to any one temperature is small, thus lessening the errors due to polymerization and decomposition.

The viscosity of the allylcatechol was measured every 20°C. from 40°C. upto 180°C., and an oil blend was prepared by mixing B.O.C. "50" and "H.S.D." oils in proportions of 3 to 2, so as to have the same viscosity as the allylcatchol in the middle of this temperature range, *i.e.*, at 110°C. This adjustment helps to keep down the corrections for difference of viscosity between the allylcatechol and the oil blend, which are seen in Table 5 below to be less than 10% at the extremes of the temperature range. Since it was desired to measure $-(\partial\nu/\partial x)_{x=0}$ and $-\Delta\nu_m$, most of the observations were in the first instance made with concentrations of allylcatechol between 0% and 40% by weight, only one mixture being made in the range 40% to 100%. The quantity of allylcatechol available barely sufficed for these measurements, because (a) the capacity of the viscometer was about 11 c.c. and (b) fresh oil and allylcatechol had to be used for each mixture in order to avoid error due to increase in viscosity consequent upon heating which is of the order of 3% per heating in the present case. Each mixture was prepared by weighing out the constituents in a covered weighing bottle, which was then heated rapidly with occasional shaking to nearly 15°C. above the corresponding miscibility temperature. The clear solution was then sucked up into an air-jacketted pipette (Fig. 5) and immediately transferred into the viscometer, already fixed in the bath, which was maintained about 10°C. above

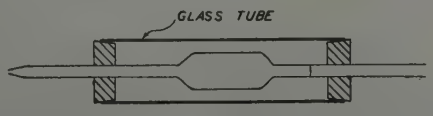


Fig. 5.—Sketch of air-jacketted pipette for transferring hot solutions into the viscometer.

the miscibility temperature. (During the transfer the temperature of the solution fell by less than 10°C., as was determined by a separate experiment.) After allowing fifteen minutes for the attainment of a steady temperature, the viscosity measurements were carried out as before, the mean of five to ten observations of the flow time being taken as the correct value. The process was repeated at all the desired temperatures, care being taken to remain at least 5 to 10°C. above the miscibility temperature, so as to avoid all possibility of separation of the two constituents inside the viscometer. (A redetermination of the (maximum) miscibility temperature with the oil blend used in the viscosity measurements gave a figure of 120±2°C. for 60% allylcatechol, which is 5 degrees lower than the value in Fig.4.) The measured viscosities are given in Table 5, and their standard deviation has been estimated as varying from 0.006 c.s. at the lower temperatures to 0.003 c.s. at the highest temperature.

Since the molecular weight of allylcatechol is 150, which differs considerably from that of the oil blend, estimated at 250 from cryoscopic measurements, the values of ν_{ideal} for an ideal mixture have been calculated in Table 5 by using molecular proportions in the formula $\nu_{ideal} = x_A \nu_A + x_B \nu_B$. The deviation $\Delta\nu$ of the measured viscosity from ν_{ideal} is calculated as $\Delta\nu = \nu_{expt} - \nu_{ideal}$, and it is seen that the values of $\Delta\nu$ are negative for small concentrations of allylcatechol, but are predominantly positive in the range 40—80% allyl catechol. This abnormal behaviour is strikingly shown in the plots of $\Delta\nu$ against concentration at different temperatures (Fig. 6 (a) and 6 (b)), in which another set of observations made with 60% allylcatechol are also included and the broken lines indicate the general trend in regions not adequately covered by experimental points. The parts of the curves near the origin (*i.e.* for less than 10% allylcatechol) are similar to those for allylphenol and allylbenzene, while the portions between 40 and 80% approach the normal behaviour only at temperatures well above 180°C.

TABLE 5.—MIXTURES OF ALLYLCATECHOL WITH MINERAL OIL.

Experimental viscosities and calculated deviations, $\Delta\nu$, in centistokes. (The standard error of the experimental values varies from ± 0.006 c.s. to ± 0.003 c.s.)

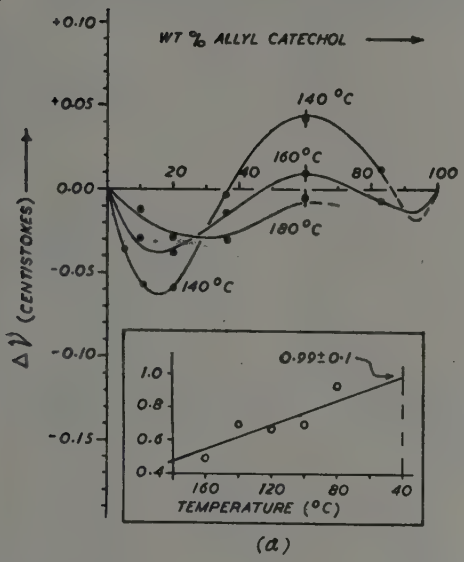
Temperature \ 100x=Wt.% allylcatechol		0	5.3	10.7	20.0	36.1	83.2	100	$-(\partial\nu/\partial x)_{x=0}$
80°C.	ν_{expt}	3.275	3.166	3.183	—	—	—	3.772	
	ν_{ideal}	3.275	3.317	3.358	—	—	—	3.772	3.5 /part
	$\Delta\nu$	0.000	-0.151	-0.175	—	—	—	0.000	
100°C.	ν_{expt}	2.293	2.217	2.170	2.218	—	—	2.322	
	ν_{ideal}	2.293	2.295	2.298	2.302	—	—	2.322	1.62/ „
	$\Delta\nu$	0.000	-0.078	-0.128	-0.084	—	—	0.000	
120°C.	ν_{expt}	1.728	1.663	1.621	1.615	1.688	1.611	1.564	
	ν_{ideal}	1.728	1.714	1.701	1.680	1.648	1.582	1.564	1.05/ „
	$\Delta\nu$	0.000	-0.051	-0.080	-0.065	+0.040	+0.029	0.000	
130°C.	ν_{expt}	1.523	—	1.421	—	1.443	—	1.330	
	ν_{ideal}	1.523	—	1.491	—	1.429	—	1.330	—
	$\Delta\nu$	0.000	—	-0.070	—	+0.014	—	0.000	
140°C.	ν_{expt}	1.360	1.307	1.269	1.241	1.257	1.189	1.155	
	ν_{ideal}	1.360	1.343	1.326	1.300	1.260	1.177	1.155	0.81/ „
	$\Delta\nu$	0.000	-0.036	-0.057	-0.059	-0.003	+0.012	0.000	
160°C.	ν_{expt}	1.096	—	1.038	1.006	0.997	0.932	0.920	
	ν_{ideal}	1.096	—	1.067	1.044	1.011	0.939	0.920	0.45/ „
	$\Delta\nu$	0.000	—	-0.029	-0.038	-0.014	-0.007	0.000	
180°C.	ν_{expt}	0.896	—	0.866	0.835	0.813	—	0.787	
	ν_{ideal}	0.896	—	0.878	0.864	0.843	—	0.787	—
	$\Delta\nu$	0.000	—	-0.012	-0.029	-0.030	—	0.000	

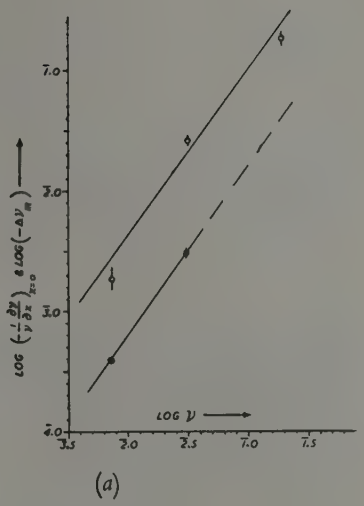
This is very surprising, since the miscibility temperature in this range of compositions lies between 115°C. and 125°C., and the experimental results therefore indicate the existence of some special effect that persists far above the miscibility temperature. The nature of this effect is being studied further, and will be discussed separately. (It is also to be noted that the minimum near 95% allylcatechol seems to be present in all the curves, and probably corresponds to the other minimum on the oil-rich side.) Here, it is sufficient to note that (a) the value of $-\Delta\nu_m$ cannot be estimated with any reliability from the above experimental data, and (b) the value of $-(\partial\nu/\partial x)_{x=0}$ appears to be nearly independent of the disturbing effect noted above, because the positive departure of $\Delta\nu$ is seen to drop very rapidly as the concentration moves away from that for the maximum, namely 60% allylcatechol. Since $-(\partial\nu/\partial x)_{x=0}$ varies very rapidly with temperature, the quantity $-(\partial\nu/\partial x)_{x=0}/\nu_{catechol}$ which has a much slower variation, was calculated from the various graphs and plotted against temperature for extrapolation to 40°C. (inset to Fig. 6 (a)). The linearly extrapolated value of $-(\partial\nu/\partial x)_{x=0}/\nu_{catechol}$ is found to be 0.99 ± 0.10. If we allow a further uncertainty of ± 0.10 due to the possible non-linearity of the actual curve, the standard error becomes ± 0.14. The extrapolated value of $-(\partial\nu/\partial x)_{x=0}$ for 40°C. is thus found to be 18.5 ± 2.6 c.s./part.

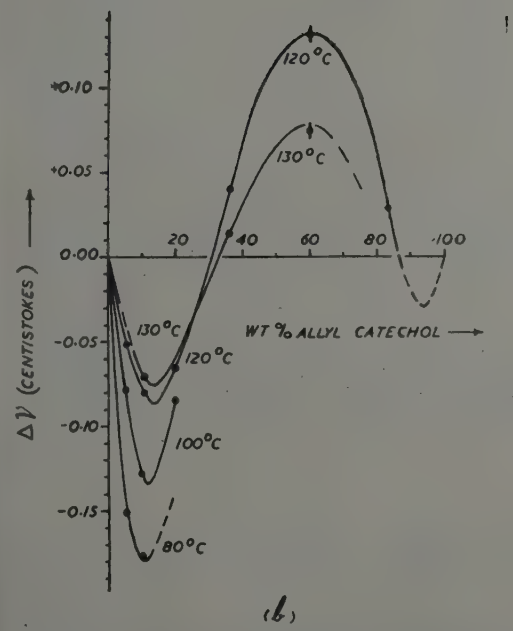
6. Conclusions and Discussion

The data obtained above on the three members of the allyl series of phenolic compounds are collected in Table 6, together with their logarithms, which are plotted in Fig. 7 (a), the short vertical lines indicating the estimated standard deviations of the corresponding measurements. It is seen that a satisfactory straight line can be drawn through the three points for $\log(-\partial\nu/\partial x)_{x=0}$, the deviation from the points being about $1\frac{1}{2}$ times the estimated experimental error. The slope of the best straight line is found to be 1.37 ± 0.07.

In the case of $\log(-\Delta\nu_m)$, only two points are available, namely those for allylbenzene and allylphenol, and the slope of the straight line joining these two points is 1.41 ± 0.07, which agrees very well with that found above for the logarithmic plot of $(-\partial\nu/\partial x)_{x=0}$, the mean







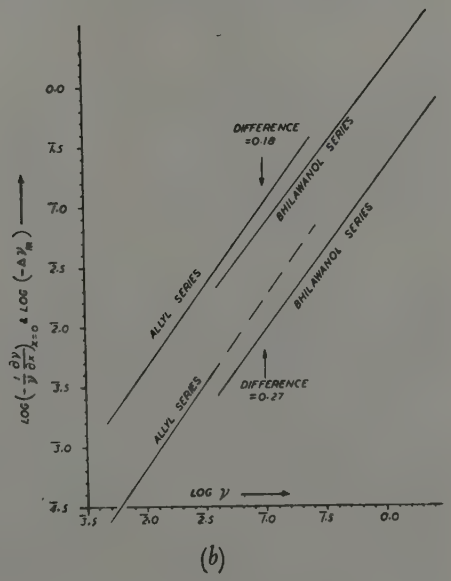


Fig. 6.—Graphs showing Δν, the departure from linearity of the viscosity of mixtures of allylcatechol with mineral oil at various temperatures (a) from 140°C. to 180°C. and (b) from 80°C. to 130°C. The inset to Fig. 6 (a) shows the extrapolation of $[-(\partial\nu/\partial x)_{x=0}/\nu_{\text{catechol}}]$ to a temperature of 40°C.

Fig. 7.—Logarithmic plots of the viscosity depressions, showing (a) the close parallelism of the linear plots for the origin slopes and the maximum depression in the allyl series, and (b) the near parallelism of the two pairs of lines for the bhilawanol series with those of the allyl series, and the upward displacement of the lines for the allyl series.

TABLE 6.—COLLECTED DATA ON VISCOSITY DEPRESSION IN THE ALLYL SERIES (VISCOSITY IN STOKES).

Compound	$\nu \times 100$	$-\left(\frac{\partial \nu}{\partial x}\right)_{x=0} \times 100$	$-\Delta\nu_m \times 100$	$\log \nu$	$\log\left(-\frac{\partial \nu}{\partial x}\right)_{x=0}$	$\log(-\Delta\nu_m)$
Allylbenzene ..	0.726	$0.18_5 \pm 0.03_5$	$0.039_4 \pm 0.025$	$\bar{3}.862$	$\bar{3}.268$	$\bar{4}.596$
Allylphenol ..	3.100	$2.6_2 \pm 0.22$	$0.30_6 \pm 0.038$	$\bar{2}.492$	$\bar{2}.418$	3.486
Allylcatechol ..	18.6	18.4 ± 2.8	..	$\bar{1}.270$	$\bar{1}.266$	..

of the two values being 1.39 ± 0.04. It is to be noted here that if mole percentages are used in place of weight percentages in calculating $(-\partial\nu/\partial x)_{x=0}$, then the slopes remain the same, but the graph for $\log(-\partial\nu/\partial x)_{x=0}$, is displaced downward by nearly 0.20 units.

In Fig. 7 (b) the two straight-line plots obtained for the ally series are compared with the corresponding linear plots for the bhilawanol series of compounds. The two plots have a common region, $\bar{2}.6 < \log \nu < \bar{1}.4$, and therefore a comparison is strictly valid in this range. It is seen in the first place that the mean slope of the lines for the allyl series is a little greater than that for the bhilawanol series, but the difference, 0.06 ± 0.05, is not statistically significant, and therefore the four lines may all be treated as being parallel (with a mean slope of 1.36 ± 0.03) within the limits of experimental error. Secondly, the lines for the allyl series are consistently higher than those for the bhilawanol series by $0.17^* \pm 0.05$, which is equal to $\log(1.48 \pm 0.16)$, whence it follows that the relative magnitude of the viscosity deperssion for the allyl series is 1.4_8 times that in the bhilawanol series.

A reasonable explanation of this increased depression is to be found in the comparatively shorter side chain in the allyl series, leading to a more dominant effect of the polar (or polarizable) phenolic nucleus. In fact, if we calculate the fraction of the molar volume occupied by the nucleus in the two series, we get for allylphenol and dimethoxybhilawanol the values, 0.8 and 0.4, respectively, whose ratio is comparable with the ratio 1.48 ± 0.15 determined above. Moreover, the above experiments show that, in the relations,

$$\left(\frac{\partial \nu}{\partial x}\right)_{x=0} \propto \nu^{n+1} \quad \text{and} \quad \Delta\nu_{max} \propto \nu^{n+1},$$

the value of 'n' is tolerably independent of the length of the side chain, the best experimental value for $n+1$ being the mean of the slopes of the graphs of Fig. 7(b), *i.e.* 1.36 ± 0.03, so that $n = 0.36 \pm 0.03$. It follows (cf. Part II) that the 'n' for the function $\psi_n = (\nu^{-n}-1)/n$ used to describe the behaviour of the above series of mixtures should also have the value 0.36 ± 0.03, instead of 0.33 obtained from the experiments on the bhilawanol series of phenolic compounds.

The anomalous increase in viscosity observed in mixtures containing 30 to 90% of allylcatechol is being studied and the results will be reported in a further communication.

* The figure given is the mean of those with 'x' as mole fraction and as parts by weight.

Acknowledgements

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QUANTITATIVE AND STRUCTURAL ANALYSIS OF KALABAGH IRON ORE BY PHYSICO-CHEMICAL METHODS WITH REFERENCE TO ITS BENEFICIATION

Part IV.—Experiments on Beneficiation of Kalabagh Iron Ore

A.H. Chotani, Sadiq A. Ahmad, Ishtiaq Ali, S.H. Rizvi and Mazhar Mahmood Qurashi

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

Introduction

The analytical and structural studies on the random and representative iron ore samples from the Kutch Khartop region of the Kalabagh ore-fields reported in earlier communications[1,2] of this series showed that the ore is of a low grade, and that its iron content is distributed almost equally over four different phases, namely hematite (α–Fe_2O_3), siderite ($FeCO_3$), limonite ($Fe_2O_3.H_2O.nH_2O$) and chamosite ($3(Fe,Mg)O.Al_2O_3.2SiO_2.nH_2O$). The present communication deals with investigations directed towards the development of an efficient and economical method for the beneficiation of this ore, which contains an average of 34% iron. To start with, a combination of the commoner ore-dressing techniques were employed in this study, and, since a representative sample was not at first available, the earlier experiments were carried out with hand-picked samples (54% Fe) supplied by Mr. A. Karim from the area leased out to him, (cf. Fig. 2 (a) in Part II). [1]

Beneficiation of Hand-Picked Samples

The hand-picked sample from the source referred to above appeared to be comparatively simple in its composition, being 75% hematite,[2] and it was therefore expected to be amenable to the usual methods of beneficiation. The samples had a very friable character, and simple crushing followed by one pass through a disc grinder with about 0.4 mm. clearance between discs gave a fine material, 60% of which passed through a 72 mesh sieve. The ground material was treated in a laboratory flotation unit, using water as the medium with very slight frothing produced by blowing air, and the heads and tailings were found to show a difference of 6% in iron content, which was considered promising. Thereafter, a second run was made with considerable air-frothing in the flotation cell. The results of these two experiments, which are given in Table 1, point to a very definite beneficiation of the ore.

Roasting followed by magnetic separation gave a 65% iron content in the heads. With these encouraging results, the work was extended to the beneficiation of the representative sample, subsequently obtained from the Kuch-khartop area,[1] and the following methods were successively tried out on it: (a) dry sieving; (b) wet screening; (c) froth-flotation, using a mixture of frothing reagents; (d) roasting; (e) wet heating.

Beneficiation of the Mean Representative Sample by Wet and Dry Sieving and Flotation

(*a*) *Dry Sieving*.—The ore sample was crushed and ground, and then sieved using standard B.S. sieves (16, 25, 30, 45, 52, 60, 72, 85, 100, 120 mesh) arranged one over the other in cascade formation, the whole assembly being shaken electrically for twenty to thirty minutes. Analysis of these sieve fractions did not show any significant variations in their iron content.

(*b*) *Wet Screening*.—Wet screening of the mean sample was next tried with B.S. sieves of 52, 60, 72, 85, 100, 120 and 150 mesh. The actual operation consisted of taking the sample on a sieve and spraying water over it from a shower. The material retained over the sieve was collected as heads and the washings were collected as tailings. Their respective iron contents were estimated,

Table 1.—Concentration of Hand-Picked Sample by Flotation.

Treatment	None	Flotation with partial frothing		Flotation with air frothing		
		Heads	Tails	Heads	Middlings	Tailings
% iron content ..	54	about 58	about 52	63 ±2	62 ±2	46 ±3

and the process was repeated with all the sieves individually. The difference in the iron contents between the heads and the tailings was in each case very small, the maximum observed being about 1%. There was, however, a marked colour change in the sample, the heads being considerably darker than the tailings. X-ray powder photographs of the heads and tails, however, gave almost identical patterns.

(*c*) *Froth Flotation.*—Using a standard frothing reagent consisting of stearic acid, washing soap, starch soluble, and calcium oxide, a beneficiation of only 1 to 2% in iron content could be attained. Simple water classification and tabling methods were also tried, but without any significant success. These results indicated that, even with recycling of material in the successive wet screening and flotation procedures, no worthwhile beneficiation and recovery of iron was likely to be attained.

These unsuccessful attempts at beneficiating the representative ore contrasted significantly with the earlier experiments made on the hand-picked sample. At this stage, therefore, it appeared necessary to review the characteristics of the two ore samples, with particular reference to their composite phases. As reported earlier,[2] the mean representative sample contains, in addition to hematite, several other equally important iron-bearing phases, namely, siderite, chamosite and limonite, whereas the hand-picked sample is mostly hematite. The hematite, siderite and limonite are all very rich in iron, while chamosite which can be considered as a ferruginous clay, contributes the gangue material in the representative ore, and any method of beneficiation can thus be effective only to the extent it succeeds in separating out this phase. Chamosite appears, however, to be intimately disseminated throughout the ore, a fact which is confirmed by its presence in almost equal proportions (estimated from X-ray powder patterns) in the heads and tailings obtained from the wet screening separation.

Thus chamosite presents the main problem in the process of beneficiation, and as suggested by some earlier workers[3] it may be possible only through chemical means. However, siderite ($FeCO_3$) and limonite ($Fe_2O_3.nH_2O$), which are both present in the ore in appreciable quantities, provide a possibility of effectively enriching the ore by its thermal decomposition into iron oxide with release of carbon dioxide and water, respectively.

Beneficiation by Dry Roasting

Small samples of the ore were roasted, out of contact with air, for half an hour at three different temperatures, namely 450°C., 600°C. and 800°C. These roasted products became black in colour, and were found to contain a magnetic component, which could be magnetically separated. The nature of the magnetic component and the relation of the phase transformations with temperature can best be observed in X-ray powder patterns, which are shown in Fig. 5 of the preceding communication.[2] It is seen that, with the increase in roasting temperature, there is an increasing transformation into the magnetic oxide accompanied by a corresponding decrease in the intensity of the lines due to hematite, siderite, limonite and chamosite, indicating the progressive breakdown of these phases. From a study of the intensity of the chracteristic lines, the percentages of the different iron bearing phases have been estimated, and are given in Table 2 together with the chemical analysis for iron. Both these estimates are probably accurate to $\pm 1\%$ iron. It may be noted that, although the intensity of the chamosite line has been considerably reduced by roasting at 600°C. and 800°C., the calculated percentages of iron in the roasted ores have had to be estimated on the basis of 30% chamosite in all the cases, due to the fact that, although the chamosite is attacked, it is not converted into one of the oxides.

This table shows that roasting out of contact with air at about 800°C. results in a marked beneficiation of the ore up to nearly 50% iron content. In order to push up the iron content still further, the roasted material was passed through a magnetic separator and it was found that because of its highly ferro-magnetic character, the material roasted at 800°C. could best be handled under the influence of the residual magnetism of the separator (*i.e.* with magnetising current switched off), when about 30% could be separated as the more magnetic component. This highly magnetic component analysed for 54% iron, and on recycling gave a fraction with an iron content of 59% but the recovery of iron in this case was quite low (about 20%).

The dry heat treatment of the ore in a non-oxidising atmosphere is thus seen to be of importance in that it can raise the iron percentage to a high value of over 50%, with practically no loss of the ore as tailings. This beneficiation is apparently brought about without release of the iron present in the chamosite. It was, therefore, considered of interest to study the effects of a related heat treatment, namely reaction with superheated steam at temperatures upto 450°C. which in the course of studies in sulphuraceous coals had been found to produce the transformation of iron pyrites into the magnetic oxide.[4]

Beneficiation by Steam-Treatment

Steam from a superheater was passed into a metal reaction vessel maintained at four different temperatures of 300°C., 350°C., 400°C. and 450°C., respectively, one kilogram of the ore being treated in each batch. These treated products were black in colour like the ones obtained on dry heating, and were found to be paramagnetic. In order to identify the various phases, and to study the course of the phase transformation, X-ray powder photographs of the samples were again taken (Fig. 1) and they showed that only a small fraction of the hematite remains unconverted into the magnetic oxide. Table 3 gives an approximate estimate of the percentages of the different iron-bearing phases in the ore as obtained from the intensities of their characteristic lines. (The chamosite contribution to the percentage of iron has (as in Table 2) been estimated on the basis of 30% in each case, although the intensity of its line shows a dimunition.) The last column indicates the percentage of material removed by playing a small horse-shoe magnet over the treated material. From a comparison of Fig. 5 of the preceding communi-

TABLE 2.—X-RAY ANALYSIS OF REPRESENTATIVE SAMPLE AFTER ROASTING.

Sample Treatment	% of the simple iron-bearing phases				Intensity of chamosite line at d=6.94A	Calculated %iron	% iron from chemical analysis
	Fe_3O_4	$FeCO_3$	α-Fe_2O_3	$Fe_2O_3.nH_2O$			
Representative ore (untreated)	—	20	15	10	30	35	34
Ore roasted at 450±40°C.	5	20	20	—	30	36	36
Ore roasted at 600±40°C.	42	—	7	—	(10)	45	46
Ore roasted at 800±40°C.	53	—	—	—	(<10)	49	50

TABLE 3.—X-RAY ANALYSIS OF REPRESENTATIVE SAMPLE AFTER HIGH TEMPERATURE STEAM TREATMENT.

Sample treatment	% of the iron-bearing phases				Intensity of the chamosite line of d=6.94A	Calculated % iron	% of magnetic part*
	Fe_3O_4 (or γ-Fe_2O_3)	$FeCO_3$	α-Fe_2O_3	$Fe_2O_3.H_2O$			
Representative ore (untreated)	—	20	15	10	30	35	—
Steam-treated at 300±10°C.	5	15	20	5	20	37	60
Steam-treated at 350±10°C.	27	7	10	—	10	39	83
Steam-treated at 400±10°C.	40	7	6	—	(<10)	46	88
Steam-treated at 450±10°C.	50	—	3	—	(<10)	48	100

* These values have been estimated through separation of the magnetic component by playing a small horse-shoe magnet over a weighed (10 g. in each case) quantity of the treated samples.

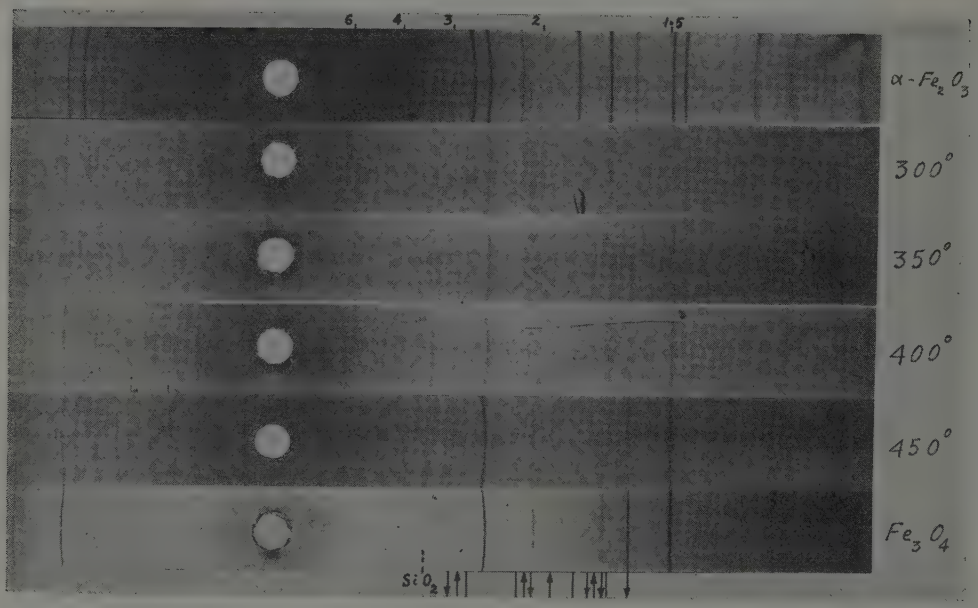

Fig. 1.—Powder patterns of steam-treated samples of ore compared with those of α-Fe_2O_3 (hematite) and Fe_3O_4. The directions of the arrows indicate increasing intensity of the corresponding lines. Steam treatment at 450°C. gives a pattern in between those for dry roasting at 600°C. and 800°C., *cf.* Fig. 5 of Part III. (Patterns taken with filtered Cr K α radiation).

cation and Fig. 1, it becomes apparent that the ore treated with steam at 450°C. is in a condition comparable with that of the dry roasted ore at 700°C. Thus a considerable reduction in the temperature of treatment can be effectd by the use of super-heated steam. Furthermore, magnetic separation can, again in this case, be useful for increasing the degree of beneficiation still further. It was found that the steam-treated samples were comparatively weakly magnetic and the residual magnetism of the magnetic separator (*i.e.* when the magnetising current was switched off) was not enough to effect a separation. This might point to the production of some γ-Fe_2O_3 as the magnetic phase in place of Fe_3O_4.

Synopsis of Beneficiation Obtained by the Simple Ore-Dressing Methods

The results of the beneficiation by the different methods that have been tried out above on this ore are summarised in Table 4, and the most suitable combinations of methods have also been indicated.

This table indicates that the maximum economically feasible limit of beneficiation of this ore by the simple methods of beneficiation is 16-18% without magnetic separation, giving a concentrate containing 50-52% iron. Further enrichment of this ore to over 56% iron is also possible by magnetic separation but in this case about half the material gets lost as tailings.

Beneficiation by Chemical Methods

Out of several chemical methods examined, nitric acid leaching has been found to be most suitable and economical for this ore. When the ore is treated with nitric acid, all the metal elements form their respective nitrates, which go into solution, leaving behind just a small fraction as insoluble residue. The solution containing iron and aluminium nitrates as its major constituents is then thermally decomposed at a suitable temperature. As there is a wide difference in the decomposition temperatures of these metal nitrates [5–8] (ferric nitrate decomposes at a low temperature of 115-135°C. as against the higher decomposition temperatures of 160°C. to 190°C. for $Al(NO_3)_3$ and 600°C. for $Ca(NO_3)_2$), it is possible to decompose just the ferric nitrate into ferric oxide, which can be separated out. In this process the other decomposition product, nitrogen pentoxide, can be easily recovered as

nitric acid by absorption in water, and recycled, reducing thereby much of the recurring consumption of nitric acid. A small-scale laboratory operation was carried out as follows.

The powdered ore (176 g.) was initially roasted at about 600°C., cooled and then mixed at room temperature (33°C.) with 600 ml. of 25% nitric acid, which was about 10% in excess of the quantity required for dissolving the total iron content of the ore. The reaction being exothermic, the temperature of the solution went up to nearly 85°C. The solution was continuously agitated and, when after a quarter of an hour, the reaction slowed down, the solution was heated for another quarter of an hour, cooled and then filtered. The filtrate containing the metal nitrates was then auto-claved in the presence of excess of water at a pressure of 30-40 lb./sq. inch, the inside temperature of the autoclave being 140-160°C. At this temperature the ferric nitrate decomposed into ferric oxide and the nitrogen pentoxide set free reacted with the excess of water to form nitric acid.

The ferric oxide was obtained as a precipitate, which was filtered, washed, and then ignited at 500°C. to remove the combined water. Some idea of the efficiency of this method can be obtained from Table 5(a), which gives the results of three separate experiments. The recovery of iron from the ore is remarkably high, being close to 80% in the present experiments, and the ferric oxide is obtained in quite a pure form as shown

TABLE 4.—SYNOPSIS OF BENEFICIATION BY THE SIMPLE ORE DRESSING TECHNIQUES.

Serial No.	Process of beneficiation tried	% enrichment of iron content	Estimated tailing loss	Possible combination of processes with % enrichment attained
1	Grinding and dry sieving ..	< 0.5	—	(a) Combination of either 2 or 3 with 4 or 5: enrichment of 16 to 18% iron content, tailing loss = 1/3
2	Grinding and wet screening ..	1-2	1/3	
3	Flotation	1-2	1/3	(b) Combination of either 2 or 3 with 4 or 5, followed by magnetic separation: enrichment of 20-22%, tailing loss = 1/2.
4	Roasting at 600-800°C. ..	12-16	nil	
5	Steam treatment at 450°C. ..	15	nil	
6	Magnetic separation of roasted material	5-8	1/3	

TABLE 5 (a).—RECOVERY OF IRON BY LEACHING WITH 25% HOT NITRIC ACID.

Expt.	Quantity of ore(g.)	Theoretical iron content(g.) of ore sample (calculated as Fe_2O_3)	Weight of (Fe_2O_3) precipitate after ignition(g.)	Percentage recovery of Fe_2O_3	
1	176	84.0	66.6	79.2%	Mean 79.4%
2	72	34.3	26.1	76.1%	
3	65	31.0	25.7	82.8%	

Table 5 (b).—Analysis of Ferric Oxide Obtained by Nitric Acid Leaching of the Ore.

Recovered Fe_2O_3 from:	Iron%	Silicon%	Aluminium%
Expt. 1, table 5 (a)	66.7	1.26	1.60
Expt. 2, ,,	69.1	0.28	traces
Expt. 3, ,,	64.8	2.80	1.08

by the analysis given in Table 5(b).

Summary

The results of the present studies in the Kalabagh iron ore may be summed up as follows:

(a) Richer than average hand-picked samples of Kalabagh iron ore are readily amenable to considerable beneficiation by routine ore-dressing methods, and yield a product having 62% to 65% iron, which can (in all probability) be smelted by one of the simple and inexpensive direct reduction processes.

(b) The mean representative sample from the Kutch Khartop area is much more difficult to beneficiate, presumably due to the finely disseminated chamosite. However, by using a combination of flotation, roasting in a non-oxidizing atmosphere (which does not liberate the iron), and magnetic separation, it is possible to attain an iron content of 52-56% with over 50% recovery.

(c) It appears likely that the tailings from the magnetic separation can be leached profitably with 25% nitric acid, from which the iron oxide can be recovered in over 95% purity by decomposition at about 150°C. The recovery of iron, by this method is found to be nearly 80%. However, it is necessary to examine the economics of this method in relation to the non-chemical beneficiation suggested at (b) above, and other iron-making processes, some of which are being investigated in these laboratories.

Acknowledgements

The authors are grateful to Dr. Salimuzzaman Siddiqui and to Mr. H.R. Amundsen for a number of very valuable suggestions, to Mr. Abdul Hai and Mr. Razaul Karim for carrying out the magnetic separation and flotation experiments, to Mr. Momin and Mr. Ain-ul-Hasan for help with the water classification, and to Mr. S.M. Ishaq Ali for setting up the ore-dressing equipment.

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A DISCUSSION OF SEVERAL DESIGNS FOR THE LARGE SCALE PRODUCTION OF LOW-COST ROOFING IN SMALL HOUSES

S. Tehzibul Hasan

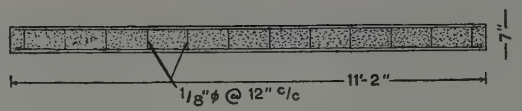
Building Research Station, Ministry of Works, Government of Pakistan, Karachi

The large scale construction of low-cost houses is of vital significance especially with reference to refugee rehabilitation. Experiments carried out by Mr. Middleton (housing expert) in the use of cement stabilised blocks have not been very successful, since, apart from the question of strength, it has been found that these walls scour away easily and develop pits on the surface. This is largely attributable to the fact that the conditions in Karachi are different from those elsewhere as the concentration and quality of alumina in the local soil does not appear to be adequate. The walls of quarters constructed with soil cement blocks are now being plastered with in order to prevent this scouring, which, however, means that there is very little economy in the total cost. Although this does not mean that further investigations into the use of soil cement blocks have been finally dropped, the best alternative, at present, appears to be the use of bajri (gravel) concrete, but with a little less cement in order to effect economy. At present cement and bajri are used in the ratio of 1:9, but a number of private houses have been constructed (many of them two storeyed) with a mix as lean as 1:18 to 1:15. However, for a quick rate of construction, it would not be desirable to use a mix leaner than 1:12.

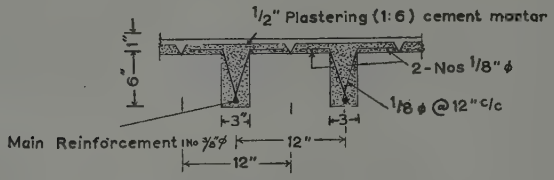
An analysis of the costs of previous constructions shows that the expenditure on the construction of walls of the refugee quarters in the Malir and Landhi colonies of Karachi is about 35% of the total cost. Some saving can indeed be made in this cost by using a leaner mix, as suggested above, without affecting the durability of the walls and the strength would be upto the specification. However the most important item on which economies are required and can be effected is the roofing which accounts for nearly half the total cost of construction. The present system of constructing the houses with R.C.C slabs is time-consuming and requires a heavy use of centring, cement and steel. The time required for fixing the shuttering and laying the slabs, and the period of curing and removal of shuttering makes it difficult to use the same shuttering more than 2 or 3 times a month. This greatly cuts down the speed of construction and at the same time increases the cost of the work. Attempts have therefore been made to design and test several types of roofing that can cut down the cost and expedite the construction of small houses. Five such designs are discussed below, and Table 1 gives a comparative statement of materials required for the important items in the construction of a single room of 10′x11′ inside dimensions.

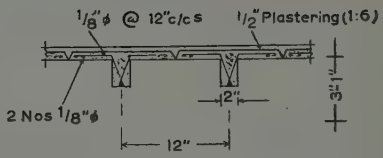
1. *Precast T-Beams Slab.*—This type of roofing reduces the quantity of concrete from approximately 50 cu.ft. required for one room (10′ x 11′ inside) and one kitchen (4′x6′ inside) to about 30 cu. ft. and that of steel from 1.7 cwt. to approximately 0.7 cwt. per refugee quarter. It is seen that this proposal will reduce not only the use of materials which are in short supply but will also cut down the time required for the construction as the problem of shuttering will be obviated. This type of roofing (Fig.1) is similar to R.C.C. precast battens and unreinforced tiles for roofing. Some of the quarters constructed in the Baldia Colony of Karachi have incorporated this type of construction. The disadvantages of this type of work are that a proper water proofing layer has to be provided on top, and that the ceiling surface at the bottom is somewhat unsightly. Experiments were also carried out using only one bar of 3/8″ in the T precast for the main room spanning 10′ clear. This type further reduces the quantity of steel required from 0.7 cwt. to 0.5 cwt. including wastage, but the handling becomes more difficult and even slight negligence of the labour in handling causes breakage of the flanges. After joining these Ts as shown in Fig. 1, this roofing gave a satisfactory result on a load test of 30 lbs. per sq. ft.

2. *Hollow Clay Block Slab.*—One of the disadvantages of the precast T-beam roofing, namely the ugly appearance of the ceiling, can be obviated by placing hollow tiles (Fig. 2) in the gaps created by T-beams placed at intervals. This is a ribbed slab construction with hollow clay blocks between the ribs instead of a solid slab, and is equivalent to providing a highly heat insulating false ceiling. It can be adopted for the middle and better classes of accommodations. Generally, the tiles are held in position by supports and the roofs are laid in situ. This type of work increases the cost of the slab as compared with the previous method, because shuttering and blocks are required. The second disadvantage of the precast roofing, *i.e.* leakage, is also

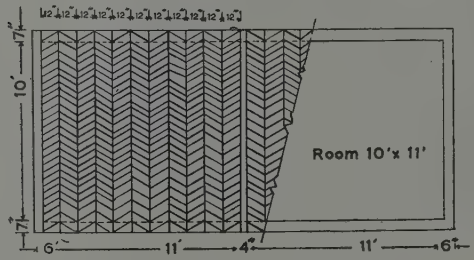


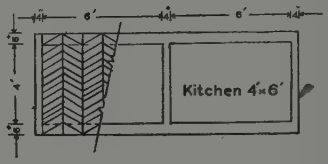
LONGITUDINAL SECTION OF PRECAST T-BEAM





Main Reinforcement 1 No 1/4" ϕ





PRECAST T-BEAM ROOFING

Fig.1

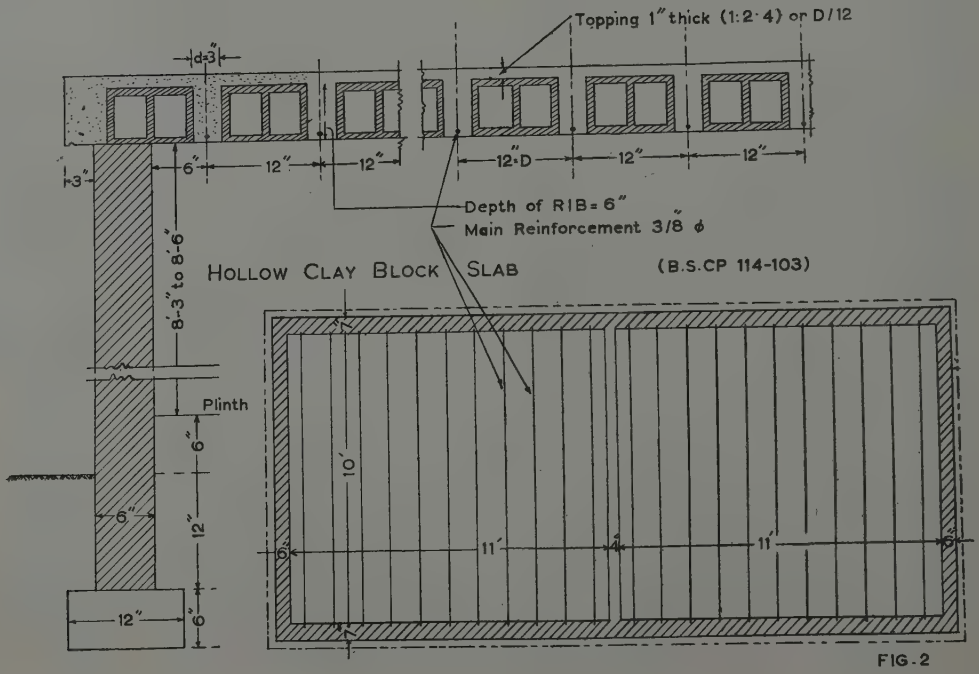


FIG.2

TABLE 1

Design	Type of roofing	Concrete (1:2:4) cu. ft.	Mild steel		Centring sq. ft.	Block masonry in (1:9) cement concrete block cu. ft.	Cost Rs.	Remarks
			As per drawing lbs.	i/c 10% washing lbs.				
	Standard R.C.C. slab	40	155	170	110	190	600	Quarters under construction at Malir, Landhi, & Drigh Village have been provided with solid R.C.C. slab.
I	Precast T-beams	26	68	75	nil	170	460	Moulds for precasting will be required.
II	Hollow clay blocks	26	46	51	50	170	500	The clay or hollow concrete blocks are required. No temperature reinforcement has been provided (Fig. 2).
III	(A) Cast-in-situ	26	78	86	110	170	480	If temperature reinforcement is not provided, the steel required will be same as in II.
	(B) Cast-in-situ	22	80	88	110	170	470	IIIA is better as the centring is easier than III B.
V	Vault plain concrete	40	nil	nil	110	193	520	No reinforcement has been provided.

Note.—Estimates of design IV have been omitted because of its limited applications in West Pakistan.

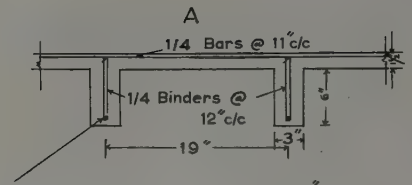
avoided as the slab is cast in situ. Hollow concrete blocks may also be used in place of clay blocks.

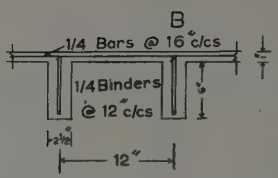
3. Cast-in-Situ Slab.—Hollow clay tiles are not readily available in quantities in Karachi, and in any case they add to the cost of construction. Therefore, it would be advantageous to lay the slab in situ without these blocks in houses constructed for refugees. The centring now becomes a bit expensive, but there is still an overall saving. A temperature reinforcement has also been provided in the slab portion (Fig. 3) to avoid cracks or leaking during the rainy season. If steel is available in the required quantity, this method will be the cheapest and the best as it avoids leakage.

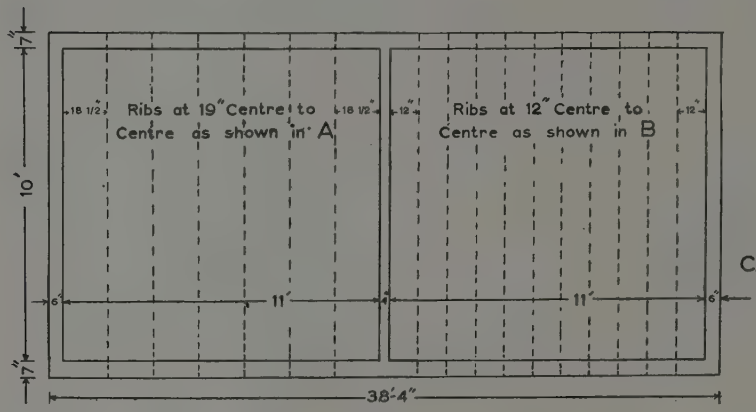
4. Precast Beams and Tiles with a Mud Topping.- A United Nations expert, Dr. O.H. Koenigsberger, who recently visited Pakistan suggested that, for houses built in West Pakistan, a 4″ earth topping is desirable to keep them cool in summer and warm in winter.

Different types of sections have been tried with 4″ mud mixed with 'bhusa' and 'gobri' mud plastering on top. Sketches of the two suitable types have been shown in Fig. 4, but the quantities required in this method are not included in Table 1 as it is not recommended for Karachi. The superstructure, according to West Pakistan conditions, shall be in 9″ thick B. Brick masonry for outer walls and 4 1/2″ thick B.B. masonry for inner walls in a set of two rooms.

5. Vault Roof.—This design shown in Fig. 5 has the special feature that no reinforcement is required. It is generally considered that this type involves costly shuttering, but if the "dhola" system as generally used in Punjab is adopted the required centring costs no more than in case of a conventional type of roofing if only a few houses are to be constructed. For large numbers of houses, steel centring will also be equally



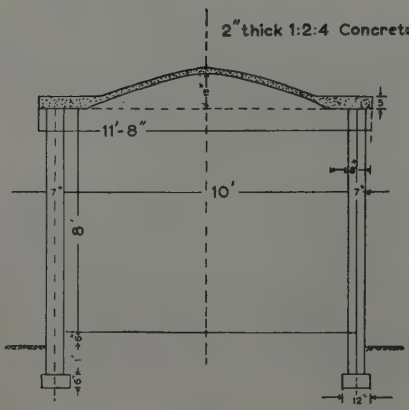


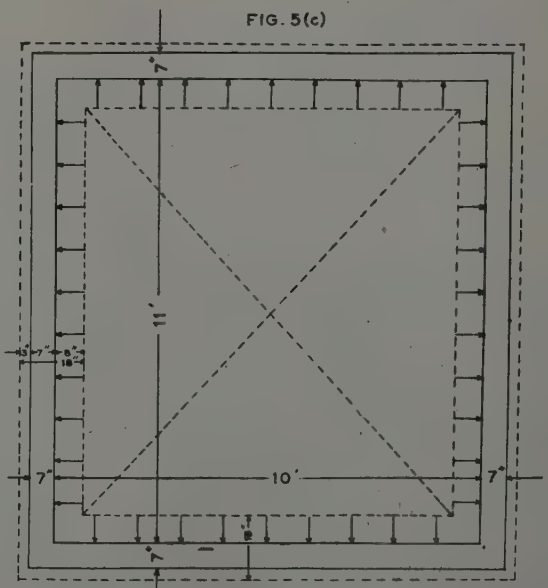


CAST-IN-SITU-SLABS

FIG. 3

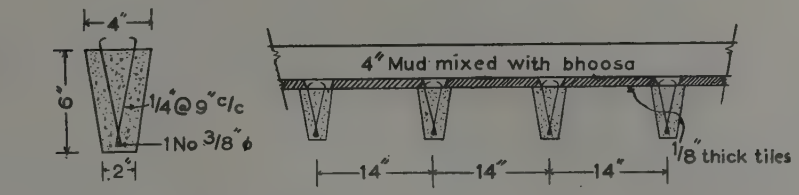
FIG. 5(c)



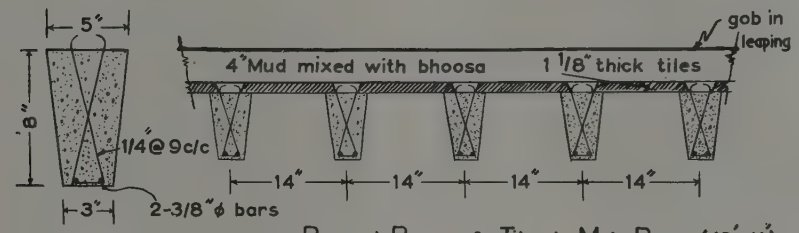


PLAIN CONCRETE VAULTED ROOF

FIGURE. 5



Detail of beam (spanning 4') Precast Beams & Tiles in Kitchen (4'×6')



Precast Beams & Tiles in Main Room (10'×11')

Detail of beam (spanning 10')

FIG. 4.a

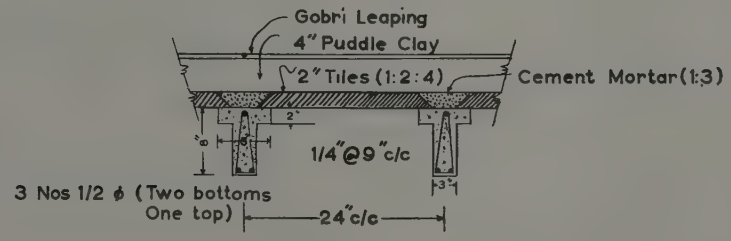


FIG.4.b

FIG 4

PRECAST ROOFING FOR WEST PAKISTAN

economical.

Mr. Chandulal C. Dangoria, Divisional Engineer, Hyderabad Improvement Board, is probably the first engineer to introduce plain cement concrete vaulted roofs to replace costly methods of construction such as R.C.C. solid slab. Later on, it was pointed out by Mr. R.G. Gokhale, Assistant Executive Engineer, C.P. W.D., that Mr. Dangoria has made some incorect assumptions in designing the vaulted roof and that this type of roofing would be unsafe and uneconomical. The following analysis however is found to lead to a workable design for a vault roof, taking our conditions into consideration, which are:

(1) Refugee quarters are to be designed for single storey.

(2) The superimposed load can be assumed to be 20 lbs. per sq. ft. as the roofs are inaccessible.

As the quarters are to be single storeyed, a 15" rise at centre has been adopted, which is not only required for reducing the thrust, but also increases, the headway. Therefore, in this type of roofing 8' high walls (above the plinth level)

will give a better appearance and greater comfort than 8′-3″ high walls in case of the refugee houses constructed with solid R.C.C. slabs.

Let A and B be a rigid frame and C an arch inside frames (Fig. 5a). Let S be the span and S/8 the rise, W be the load per sq. ft., and H.T. be the horizontal thrust and B.M. the bending moment.

(*i*) If the slab is vaulted one way only and is rigid at the ends, then

$$\text{H.T.} \times S/8 = WS^2/8$$
$$\text{or H.T.} = WS$$
$$\text{and B.M.} = \text{H. T.} \times S^2/12 \text{ lbs ft.}$$
$$= WS^3 \text{ lbs. inches}$$

(*ii*) If the slab is vaulted both ways, the B.M. will be half that calculated above, *i.e.*

$$\text{B.M.} = WS^3/2 \text{ in lbs.}$$

Thickness of arch width of the vault is limited by the modulus of elasticity of plain cement concrete, as in case of pipes under external pressure, the formula being

$$\frac{T}{S} = \sqrt{\frac{Fc}{Ec}},$$

T = Thickness of arch at crown, S=span of arch, Fc=Safe compressure stress of concrete 600 lbs. per sq. inch, Ec=20,00,000 lbs. per sq. inch.

Thus $\frac{T}{S} = \sqrt{\frac{600}{2 \times 10^6}} = \frac{1}{56}$, or say $\frac{1}{60}$

Therefore, a 2″ thickness is adopted in the present case.

Superimposed load = 20 lbs. per sq. ft.

Dead load (i/c finishing etc.) = 30 lbs.
Therefore W = 50 lbs.

$$\text{B.M.} = \frac{50 \times 10^3}{2} = 25000 \text{ in lbs.}$$
$$= Fc \times \frac{bd^2}{6}$$

Fc = 100 lbs per sq. inch in 1:2:4 concrete

Assuming b=5″, $100 \times 5 \times \frac{d^2}{6} = 25000$

$\therefore \quad d^2 = 300$

or $\quad d = 17.3''$

The thickness provided is 18″ as shown in Fig. 5(b) and Fig. 5(c) for a room of 10′ × 11′ inside.

STUDIES ON ABROMA AUGUSTA LINN. PART I

SADIQ ALI, AHMAD MUBASHAR AHSAN AND GEORGE HAHN

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

Abroma augusta Linn. (Sterculiaceae), called "olat kambal" in Urdu and "devil's-cotton" in English, grows throughout the hotter parts of India and is mentioned in Chopra's and subsequently in Nadkarni's Indian Materia medica. According to these authors the roots contain an alkaloid in very minute quantity (0.01%) besides a fixed oil, resins and water soluble bases. The leaves and stems are reported to be demulcent, the root bark emmenagogue.

Some time after having started the present investigation the authors came to know that Srivastava and Basu[1] had succeeded in isolating from the roots a hygroscopic water soluble alkaloid which they named "abromine" m.p. 283—85°C. (dec.). Its chlorhydrate showed no rotation in aqueous solution. Based on the analysis of the chlorhydrate (C, 42.56; H, 8.34; N, 8.0; Cl, 24.7) they put up the molecular formula $C_6H_{13}NO_2.HCl$. Besides this alkaloid, they isolated a phytosterol m.p. 153-57°C., to which they attributed the formula $C_{30}H_{52}O_2$. This sterol too did not have any optical activity in benzene solution. The values found were C, 81.21; H, 11.56. Its acetate melted at 123-128°C.

Because *Abroma augusta* is not easily available in the West Pakistan market, only one batch of 20 kg. could so far be investigated. The results obtained differ from those reported by Srivastava and Basu and are published as a preliminary account.

The coarsely powdered dry roots, the storage time of which could not be determined, were exhaustively extracted with petroleum ether b.p. 60-80°C. and this extract submitted to adsorption analysis on alumina according to Brockmann (E. Merck) with chloroform as eluate, fractions of 30 ml. each being collected. According to the behaviour of their residues, fractions 1-9 were combined into group I, while fractions 10-20 formed group II. A fairly pure, crystalline substance appeared with the fraction 21, and finally the fractions 22-50 were united into group IV. Group I contained as the main substance laths m.p. 247-50°C. (ethyl acetate) showing an $[\alpha]_D^{35.5} = -26°$ in 1% chloroform solution. Found, C, 84.0; H, 11.67; O, 4.26 m.w. (Rast camphor), 376. Digitonin, Liebermann, Burchardt and Salkowsky tests were negative. The infrared spectrogram furnished a strong band at 1700 cm.$^{-1}$ indicating a carbonyl group. According to the analytical findings a formula within the range of $C_{25\text{-}30}H_{42\text{-}50}O$ had to be taken into consideration in which only the presence of one oxygen atom was certain as indicated by the carbonyl group. In agreement with this, an oxime m.p. 290-294°C. and a 2,4-dinitrophenylhydrazone could be obtained. The comparison of these data with those for the already known sterols, triterpenes, etc. show that the compound is friedelin, which was isolated by Chevreul,[2] Istrati et al.,[3] and Friedel.[4] In order to clearly identify the substance obtained from *Abroma augusta* with friedelin from cork, one kg. of cork stoppers were extracted according to the method of Ruzicka et al.[5] and Brunn,[6] and friedelin, which is more soluble in the common solvents and is present in bigger quantities, was isolated. The friedelin obtained from cork corresponded with that obtained from *Abroma augusta*, as shown in Table 1.

TABLE 1

	m.p.	$[\alpha]_D$	Shape of crystals
Friedelin (cork)	247-50°C.	− 22°	laths
Friedelin (*Abroma augusta*)	247-50°C.	− 26°	laths

The identity was finally confirmed by the infrared spectrogram in Fig. 1.

Further investigations are in hand to ascertain whether cerin is also present. Being sparingly soluble in chloroform it may occur in group IV.

Repeated recrystallisation of the combined fractions 20, group II, revealed that it consists of a mixture of several constituents, difficult to separate by crystallisation. Therefore the several parts received according to Table 2 were again submitted to adsorption analysis on alumina with benzene as eluate. At least two sterols could be isolated from the mixture. They may be named abromasterol A and B as long as it cannot be ascertained that they are indentical with any known ones.

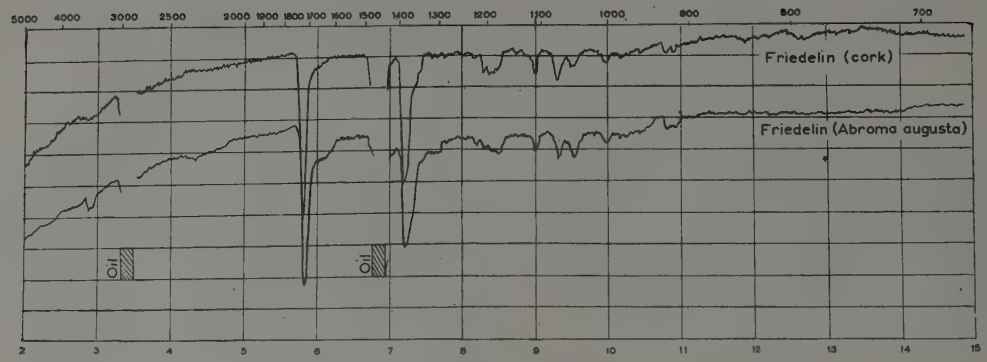


Fig. 1.—Infrared spectrograms.

Sterol A, m.p. 126-128°C. $[\alpha]_D^{35}$ –26° in 1% chloroform solution, [found: C, 82.56; H, 11.98; O,5.46, m.w. 304 (Rast, camphor)] fits into the range of C_{19-22} H_{32-38} O. A strong band at approximately 3500 $cm.^{-1}$ in the infrared spectrogram indicated a hydroxyl group. In agreement with this, an acetyl derivative could be prepared which melted at 110-112°C.

Sterol B could be clearly separated from sterol A due to the fact that it remained completely adsorbed on alumina during the elution with benzene, which brought down sterol A. Only after adding ether to the benzene could sterol B be eluted. However it was still mixed with another constituent, from which it could only be separated by high vacuum sublimation. It crystallises in needle shaped aggregates melting at 135-137°C. The benzoyl derivatve melted at 138-140°C. Its melt on resolidification showed a play of colours, chiefly blue, which is suggestive of β-sitosterol benzoate

Experimental

Extract of Abroma Augusta.—20 kg. of the air-dried roots were shredded, coarsely powdered and exhaustively extracted with petroleum ether (b.p. 60-80°C.) by percolation at room temperature (30°C.). On removal of the solvent, a red oily mass (30.5 g.) remained, which on standing over-night deposited increasing amounts of crystalline material.

Notwithstanding the presence of these crystals, 15.4 g. of that crude mass was dissolved in chloroform (25 ml.) and passed through a column of alumina according to Brockmann (E. Merck) of 45 cm. length, 3.5 cm. breadth containing 470 g. Elution was done with chloroform, fractions of 30 ml. each were collected and the solvent removed.

After preliminary examination, the fractions were combined in the following groups:

Group I, fractions	1-9	10.8 g.	73% yield
Group II, fractions	10-20	2.9 g.	19% yield
Group III, fractions	21	0.011 g.	—
Group IV, fractions	22-50	0.41 g.	2.7% yield

Investigation of Group I. Isolation of Friedelin.—On adding petroleum ether to the crude oily mass, a crystallisate was obtained (0.82 g.), which on repeated recrystallisation from ethyl acetate gave laths of constant m.p. 247-250°C. They were readily soluble in chloroform, moderately so in benzene, and sparingly soluble in petroleum ether, alcohol, ether and acetone. $[\alpha]_D^{35} = -26°$ in 1% chloroform solution. Digitonin, Liebermann, Burchardt and Salkowsky tests were negative.

Calculated for C_{30} $H_{50}O$: C, 84.44; H, 11.81; O, 3.75; m.w., 426.7. Found: C, 84.00, H, 11.67; O, 4.26; m.w., 376 (by camphor).

Oxime.—To 0.8 g. of hydroxylamine hydrochloride dissolved in 5 ml. of alcohol, 0.7 g. of potassium hydroxide in 5 ml. of alcohol was added and this solution was refluxed together with 200 mg. of the substance of m.p. 247-50°C. for two hours. After cooling it was poured in water and acidified with hydrochloric acid. The substance coming out was filtered by suction, washed and dried. Yield, 140 mg. Recrystallised from ethyl acetate and benzene, m.p. 292°C.

2,4-Dinitrophenylhydrazone.—200 mg. of the substance of m.p. 247-50°C., was dissolved in 5 ml. of glacial acetic acid, the solution of 0.2 g. of 2,4-dinitrophenylhydrazine in 2 ml. of glacial acetic acid added and refluxed for half an hour. On cooling orange coloured crystals were deposited. Recrystallisation from benzene furnished the pure product melting at 296-297°C. (dec.).

Friedelin from cork.—One kilogram of cork stoppers were exhaustively extracted as such with ethyl acetate in a Soxhlet apparatus in order not to damage them. The extract was processed according to the description of Ruzicka et al.[5] and Brunn.[6] The finally obtained friedelin, m.p. 247-50°C., showed no difference in appearance and no depression when mixed with the main substance from the first group of *Abroma augusta*. The final confirmation gives Fig. 1 where the infrared spectrograms of both substances are to be seen side by side.

Investigation of Group II. Isolation of Abromasterol A.—By treatment of the crude material (2.9 g.) with petroleum ether, a crystallisate was obtained (1.53 g.), which was further recrystallised according to Table 2.

TABLE 2

1.53 g. from petroleum ether

↓

Crystallisate 1 ——→ mother liquor 1
0.946 g. again from petroleum ether

↓

Crystallisate 2 ——→ mother liquor 2
0.48 g. again from petroleum ether

↓

Crystallisate 3 ——→ mother liquor 3
0.018 g., m.p. unsharp 140°C. 0.288 g.

Combined 1.056 g.

TABLE 3

Fraction	Volume of fraction in ml.	Weight of residue in g.	m.p.°C. Kofler block	Remarks
1	11	0.063	Sublimes at approx. 180.	Needle shaped crystals solubilities similar to friedlin.
2	10	0.026	Partly subl. at 180. Rest melts at 190-200	Needle shaped crystals mixed with hexagonal ones
3	15	0.016	Oil	Yellow
4	10	0.016	Oil	Yellow
5	10	0.043	118-142	Light yellow wax containing clusters of needles
6	10	0.049	117-125	Colourless waxy substance containing clusters of needles.
7	10	0.061	123-127	,,
8	10	0.075	123-127	,,
9	10	0.074	125-128	,,
10	10	0.072	125-128	,,
11	10	0.098	126-130	,,
12	10	0.086	127-129	,,
13	10	0.051	120-130	,,
14	15	0.010	118-130	,,
		0.074		

The combined residues of mother liquors 1 and 2 (1.056 g.) were dissolved in 50 ml. of alcohol, filtered from an insoluble part, which turned out to be friedelin, and brought to dryness again. Its solution in 10 ml. of benzene was submitted to adsorption analysis again on an alumina column (30 g., 34 cm. length, 0.9 cm. breadth), the elution being done with benzene. The results are given in Table 3.

On repeated recrystallisation of the mixed residues of fractions 10, 11 and 12 (256 mg.) from alcohol, colourless plates (112 mg.) were obtained with the constant m.p. 126.5°C. (Kofler block).

They were readily soluble in chloroform, less so in alcohol, benzene, acetone, ether, ethyl acetate and petroleum ether. On drying at 100°C. over phosphorus pentoxide no loss in weight was observed. $[\alpha]_D^{35} = -26°$ in 1% chloroform solution. It gave positive Liebermann, Burchardt, Salkowsky and digitonin tests.

Calculated for the range $C_{19-22}H_{32-38}O$; C,82.54-82-95; H,11.66-12.03; O,5.79-5.02; m.w. 276.5-318.5. Found: C,82.56; H, 11.38; O,5.46, m.w., 304 (camphor).

Abromasterol A Acetate.—75 mg. of sterol A were kept standing for 14 hours at room temperature (30°C.) with acetic anhydride in the presence of a drop of pyridine. Poured in water and kept until the anhypride was hydrolysed, and finally filtered by suction. m.p. 110-112°C. from alcohol

Isolation of Abromasterol B.—Attempts to further purify the residue of mother liquor 3 in Table 2 (0.268 g.) by fractional crystallisation and adsorption analysis on alumina were unsuccessful. It was noted that this fraction was completely adsorbed by alumina from petroleum ether and benzene solutions as distinct from sterol A, which was eluted with benzene. This fraction, which could only be eluted by adding ether to the benzene, was found to consist mainly of two types of crystals: one needle shaped m.p. 135-137°C. (Kofler block), which showed some sublimation, the other plate or leave type, in much smaller amounts. The whole fraction therefore was subjected to sublimation in high vaccum (0.01 mm.), when 70 mg. of the needle shaped substance was obtained. As there was a considerable decomposition in spite of the use of high vaccum, the process was not repeated for further purification. Instead, on benzoylation of the sublimate by treatment with benzoyl chloride and pyridine at room temperature colourless plates (25 mg.) m.p. 138-140°C. (Kofler block) could be obtained. They were sparingly soluble in alcohol, readily so in chloroform and ethyl acetate. The melt of the subsance exhibited, play of colours, chiefly blue, on resolidification which is suggestive of β-sitosterol benzoate.

Group III fraction 21, consisting of 11 mg. showed a fairly sharp melting point at 178-184°C. but could not be purified further due to its small quantity.

The group IV fraction (0.41 g.) is under investigation.

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STUDIES ON MARINE EDIBLE (TELEOSTII) FISHES

Part 1.—Distribution of Oil and Vitamin A in the Skin, Flesh and Liver of Edible Fishes of Karachi Waters

A. Hameed Khan and S. Abdul Haq

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

Introduction

In the course of earlier work on the utilisation of shark liver oil as a source of vitamin A,[1] it was noted that the liver oil of sharks caught around the Karachi and the Mekran coast was several times richer in its vitamin A content than that from sharks landed around Bombay. This has been attributed to the super-abundance of prawns and shrimps on the Karachi coast.[2] It was, therefore, considered of importance to extend this study to the edible marine fishes of these waters, specially because these fishes constitute a major item in the diet of the indigenous population around these coasts. Statistical data collected by the Department of Fisheries, Government of Pakistan, Karachi, indicate that the annual landing of edible fishes around the Karachi coast is approximately 33 thousand tons out of which 7,000 tons are consumed by the local population and the rest is either cured or utilised for manufacturing fishmeal. With regard to their palatability, these fishes have been grouped into the following three main classes:—

Class	*Local names*
A	Surmai, rawas, white pomfret and black pomfret.
B	Sua, aal, boi, palla, hira, dothar and dawan.
C	Mushka, khagga and kund.

Fishes belonging to class "A" are the most delicious, but also the most expensive.

Table 1.—The Distribution of Vitamin 'A' in Liver, Flesh and Skin Oil.

Name of the species	English popular name	Local name	Liver		Flesh		Skin	
			p.c. of oil	Vit. A per g. of oil I. U.	p.c. of oil	Vit. A per g. of oil I. U.	p.c. of oil	Vit. A per g. of oil I. U.
Clroinemeus Tolooparah	Leather jacket	Aal, Mathiyamach.	4.2	343,390	0.12	4,683	0.8	5610
Mugil Speigleri	Grey Mullet	Boi	2.3	5,616	0.806	500	3.0	193
Thynnus thunnina	Tuna	Dawan	3.7	201,058	0.9	1,07	1.3	5000
Pristipoma olivaceum	Pomadasid	Dhother	2.4	75,000	0.42	870	2.6	traces
Lutianus Rivulatus	Snapper	Hira or Muyyo	7.5	100,000	0.7	267	3.7	7842
Clupea Ilisha	Shad or Hilsa	Palla	9.9	620	12.8	354	15.4	nil
Sciaena Dicanthus	Drums or Croakers	Sua	18.2	26,476	1.2	nil	5.7	nil
Pelamys Chilensis	Striped Mackeral	Surmai or Kergan	1.5	10,140	0.08	nil	0.607	2637
Polynumus Indicus	Threadfin	Rawas or Luckwa	2.5	156,437	0.055	3145	1.3	545
Stromateus Sinensis	White Pomfret	Achchopitho or Paplet	2.9	20,900	1.3	negligible	5.8	nil
Parastromateus Niger	Black Pomfret	Kalapitho or Kalachanda	3.9	16,213	2.8	65	11.3	nil
Arius Serratus	Cat fish	Khagga	2.2	21,000	0.105	nil	0.49	nil
Platycephalus Scaber	Flathead	Khokker	24.9	2,836	0.14	negligible	0.4	45,819
Otolithas Ruber	Drums or Croakers	Mushka	3.08	20,900	0.66	770	4.2	traces

Investigation of some of the important fishes, belonging to all the three groups mentioned above, is of particular significance in so far as the data obtained can be used in regulating the composition of our daily diets with respect to vitamin A, proteins and fats, etc.

The present paper deals with the distribution of vitamin A in the skin, flesh and liver of the fishes. Although the skin represents a very small portion of the body it has been included in the analysis because of a possible concentration of the oil and vitamin A in the skin.

Extraction of Oils

The oil was obtained by grinding the appropriate tissue with anhydrous sodium sulphate and repeatedly extracting with ether. The solvent was completely distilled off, the last traces being removed under vacuum.

Estimation of Vitamin A

A portion of the fresh oil was saponified, the unsaponifiable matter after the removal of the alkali was taken up in isopropyl alcohol and the vitamin A was estimated spectrophotometrically.[3]

The quantity of vitamin A was also estimated by means of the Carr-Price[4] (antimony trichloride) colour reaction, the blue colour produced being measured in a Hilger photoelectric colorimeter using filter 70.

Results for the distribution of vitamin A in the oil from the skin, the flesh, and the liver of 14 very common *teleostii* fishes are given in Table 1, while Table 2 shows the amount of vitamin A per 100 g. of flesh and per g. of the liver in various fishes.

Table 2— Showing the Vitamin 'A' Content of the Flesh and the Liver.

Name of the species	Local name	Vitamin A in flesh I.U./ 100 g.	Vitamin A in liver I.U./g.
Clroinemus Tolooparah	Aal	421	14422
Mugil Speigleri	Boi	400	129
Thynnus Thunnina	Tuna or Dawan	963	7439
Pristipoma olivaceum	Dother	345	1800
Lutianus Rivulatus	Hira	186	7500
Clupea Ilisha	Palla	4531	61
Sciaena Dicanthus	Sua	—	4818
Pelamys Chilensis	Kergan	—	152
Polynumus Indicus	Rawas	172	3910
Stromateus Sinensia	Achchopitho	—	606
Parastromateus Niger	Kalapitho	182	632
Arius Serratus	Khagga	—	462
Platycephalus Scaber	Khokker	—	706
Otolithes Ruber	Mushka	508	643

Discussion

The results in Table 1 show that some of the fishes examined, *e.g.*, aal, khokar, sua, etc., have oily livers, the muscle being very low in fat. On the other hand, some fishes such as palla have relatively small livers with little oil in them, but have very oily muscle tissue. This observation has also been made by other workers, who have noted that fishes like cod, haddock, etc., have fairly large livers rich in oil, but their flesh is very poor in oil content, while salmon has a relatively small liver and very oily muscle tissue.[5]

The livers of aal, dawan, dothar, hira and rawas, have an exceptionally high vatamin A content, the liver oil from aal having as much as 300,000 I. U. of vitamin A per g. As with sharks, this can most probably be attributed to the eating habits of these fishes. For instance, aal, dawan, hira, etc., with high vitamin A contents are mainly carnivorous, while boi, mushka etc. with low amount of vitamin A are plankton eaters.

It will be seen from Table 2 that, the flesh of 'A' class fishes is poor in vitamin A, while their livers are quite rich in it. On the other hand, 'B' and 'C' class fishes have most of their vitamin A in their flesh, the livers containing very little of it. The flesh of palla has a very high vitamin A content with 4531 units per 100 g. of flesh, as

against 963 units in tuna, which is the next lower in this respect (*vide* Table 2). It is also significant that palla is very popular amongst the poorer classes of Sind.

The abnormally high values of vitamin A in the skin of some of the fishes is rather peculiar and is being further investigated. Since in most fishes fat is found in a thin tissue immediately under the skin, and also in the liver and the flesh, it is possible that the high amount of fat in the skin of these fishes might account for greater vitamin A content (Table 1). Further work on *teleostii* fishes of Karachi waters is in progress.

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EXAMINATION OF SAFFLOWER OIL FROM INDIGENOUS SOURCES WITH REFERENCE TO ITS USE IN THE MANUFACTURE OF PAINTS AND VARNISHES

MOHAMMAD ASLAM

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

Introduction

Safflower has become increasingly important in recent times because it is exceptionally rich in linoleic acid. The safflower oil contains 75-78% linoleic glyceride with little or none of the linolenic glyceride, which gives it excellent non-yellowing and colour retention properties, and makes the oil very suitable for the manufacture of oil-modified alkyd resins and similar products. The oil itself is reported[1] to dry to a hard film within eight hours in the presence of 0.03% Co and 0.3% Pb, and can therefore be used to advantage in place of linseed oil in the manufacture of oil paints.

Safflower oil is obtained from the seeds of "*carthamus Tinctorius*," a thistle-like plant which has been cultivated in India, China and Egypt, since ancient times for the production of a red-dyestuff (carthamin) obtained from the florets, and also for the extraction of edible oil from the seeds. As carthamin has now been compeltely replaced by aniline colours in the textile field and finds only a limited use in cosmetics, the oil-bearing varieties of this plant are now being especially cultivated. They yield little or no dye, and their commercial value lies mainly in the oil. Whereas the seeds from plants grown for the carthamin dye had only 22—28% of oil, certain varieties recently developed in Australia, in the mid-western states of U.S.A., and in some other countries, have an oil content as high as 38%.[2] Work on the cultivation of such varieties has also been more recently carried out by Messrs. Sind Land Development Farms. Some of the varieties developed in the course of this work have been examined at the Central Laboratories with special reference to the industrial uses of the oil, and the results are given in this paper.

The Content of Oil and its Composition

The oil contents of four varieties of seeds are given in Table 1 and the characteristic constants

TABLE 1

Varieties	Oil content%		Moisture
	Whole seed	Kernel	
Farmseed ..	37.3	62.0	6.0
Fatisa ..	35.3	62.1	6.1
Shambat ..	35.7	63.4	5.3
Debra ..	37.8	62.5	5.5

TABLE 2.—CHARACTERISTICS OF THE OIL.

Characteristics	Variety			
	Farm seed	Fatisa	Shambat	Debra
Specific gravity @ 28°C.	0.9182	0.9183	0.9181	0.9181
Refractive index @ 25°C	1.4727	1.4723	1.4727	1.4725
Viscosity @ 30°C. (centistokes)	42	42	42	42
Acid value	1.9	1.4	4.7	1.9
Saponification value	192	190	196	191
Iodine value (Hanus)	136	142	136	140
Thiocyanogen value	77	78.2	77.3	77.9

TABLE 3.—COMPOSITION OF FATTY ACID GLYCERIDES.

Glyceride	Variety			
	Farmseed	Fatisa	Shambat	Debra
Linoleic glyceride %	68.0	73.6	67.5	71.8
Oleic glyceride %	20.9	16.7	21.6	18.4
Saturated glycerides %	11.1	9.7	10.9	9.8
Saturated glycerides % (Bertram's method) ..	12.2	10.3	11.5	10.7

TABLE 4.—DRYING TIMES (IN HOURS) OF SAFFLOWER OIL FILMS AT 28—30°C.

Drier in oil	Farmseed-shambat			Fatisa-Debra		
	Touch dry	Hard dry	Tack free	Touch dry	Hard dry	Tack free
A. Soluble driers						
0.5% Pb	48	—	—	48	72	—
0.5% Mn	24	36	—	12	16	72
0.25% Mn	36	48	—	14	18	—
0.25% Co	6	24	—	4	16	—
0.3% Pb+0.03% Co ..	12	18	—	8	14	48
0.3% Pb+0.1% Co ..	7	16	—	4	8	48
0.5% Pb+0.1% Co ..	7	16	—	4	8	36
B. Drier metals cooked in oil						
0.5% Pb	28	60	—	24	36	—
0.5% Mn	14	28	—	9	12	60
0.25% Mn	26	36	—	11	15	—
0.3% Pb+0.1% Co ..	5	12	—	3	6	36
0.5% Pb+0.1% Co ..	5	12	—	3	6	30

The minus sign '—' denotes that the film does not become tack-free.

of the oil in Table 2, while Table 3 shows the composition of the constituent fatty acid glycerides.

The composition of the fatty acids has been determined from the iodine and thiocyanogen values. In these calculations, no unsaturation greater than that of linolenic acid is assumed to be present. The absence of linolenic acid was confirmed by determining the proportion of saturated fatty acids and calculating the percentage of linolenic acid by using the following equation, which gave a negative value.

$$\text{Linolenic acid}\% = 1.5637 \times \text{T. V.} - 0.0780 \times \text{I. V.} + 1.3271 \times \text{S} - 132.71$$

Where T. V. is thiocyanogen value, I. V. is iodine value and S is proportion of saturated fatty acids.

Drying Properties of the Oil

The drying properties of the oils have been studied under the two following conditions:

(a) after addition of liquid driers of known metal concentration, the driers being in the form of stabilised solutions of lead, manganese and cobalt rosinates in white spirit.

(b) with the incorporation of driers obtained by cooking the metallic oxides or acetates into the oil.

Test samples of oil containing the required concentration of driers were painted on glass panels and the time taken for the films to dry to touch, to hard dry, and to become tack-free (all at room temperature) was noted.

For this study, the oils were divided into two batches, the first batch consisting of 'Shambat' and 'Farmseed' varieties, of iodine value 136, and the second batch of 'Debra' and 'Fatisa' varieties, of iodine values 140 and 142 respectively.

The above results show that the drying properties of the oil from 'Fatisa' and 'Debra' varieties are satisfactory with a drier containing 0.5% lead and 0.1% cobalt. With the same driers, 'Farmseed' and 'Shambat' varieties fail to become tack-free, and cannot therefore be used as substitutes for linseed and other drying oils in the manufacture of paints.

TABLE 5.—LOAD IN GRAMS FOR RUPTURING OF FILMS OF OLEO-RESINOUS VARNISHES INCORPORATING (a) SAFFLOWER OIL (b) LINSEED OIL.

Oil length gallons per 100 lbs. resin.	Load in g.	
	Safflower varnish	Linseed varnish
15	280–290	250–260
25	320–330	300–310
35	320–330	310–320

TABLE 6.—WATER RESISTANCE PROPERTIES OF OLEO-RESINOUS VARNISH FILMS.

Oil length (gallons per 100 lbs. resin)	Oil	Time for disappearance of haze after				
		One hr. dip	Two hr. dip	Four hr. dip	24 hr. dip	48 hr. dip
15	Safflower	unaffected	unaffected	unaffected	1—1½ hrs.	6—8 hrs.
	Linseed	"	"	"	2—3 hrs.	10—12 hrs.
25	Safflower	"	"	"	8—10 hrs. slightly affected.	presists after 24 hrs.
	Linseed	"	"	20 minutes	persists after 24 hrs.	whiteness, persists after 24 hours.
35	Safflower	"	10 minutes	30 minutes	persists after 24 hrs.	whiteness, persists after 24 hours.
	Linseed	"	30 "	1 hr. slightly affected.	persists after 24 hrs.	whiteness, persists after 24 hours.

Tests on Oleo-Resinous Varnishes incorporating Safflower Oil

Oleo-resinous varnishes of '15', '25' and '35' gallons oil length have been prepared and their properties compared with corresponding linseed oil varnishes. All the varieties of safflower oil examined have been found to be suitable for this purpose. The loads for rupturing films of the afore-mentioned varnishes on a standard scratch-test apparatus have been determined, and the values are reported in Table 5. The water resistance properties are given in Table 6.

It appears from the two tables that in both series of tests, safflower oil varnishes are slightly superior to those based on linseed oil.

Conclusions

The oil content of the different varieties developed by Messrs. Sind Land Development Farm has been found to compare favourably with the best reported figures in the literature. The present work shows that 'Fatisa' and 'Debra' varieties can be used satisfactorily either as drying oils or for the manufacture of oleo-resinous varnishes. In fact, the performance of the varnishes based on safflower oil is found to be somewhat superior to that for linseed oil varnishes. The extensive cultivation of safflower seed should therefore be seriously considered in view of the non-availability of linseed and other suitable drying oils in the country.

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A NEW RECORD OF ALTERNARIA NELUMBII ENLOWS AND RAND IN THE INDO-PAKISTAN SUB-CONTINENT

A.B. Mallik and S.A. Qadir Junaidi

Department of Botany, University of Karachi, Karachi

In October, 1957, a few leaves of *Nelumbium speciosum* were collected from a pond in Sukkur, Sind, and were found to show spots of varying sizes scattered all over the surface. The spots were light to deep brown in colour (deeper colour on the upper surface and lighter on the lower surface), and were mostly round, oval, elongated or irregular in shape, measuring 3x2 mm. to 10x7 mm. These spots were at first very minute but gradually enlarged in size. Microscopic examination revealed that the fungus responsible for causing the disease was *Alternaria*.

The literature on this subject shows that in the whole of the Indo-Pakistan sub-continent there is no record of this fungus on the particular host examined, although in North America, *Alternaria nelumbii* Enlows and Rand has been reported on this host.

In the present investigation, the fungus was studied in culture medium (P.D.A.) as well as on the host and the following observations were made, cf. Figs. 1 and 2. Fructification on upper surface, conidiophores short, sepatate, light brown in colour, 65 to 130μ ×3.8 to 5.9μ. Conidia muriform deep brown when matured, walls slightly coriaceous, oblong to obclavate, rarely globose measuring 25 to 56 μ× 10 μ, beak slightly longer on host leaves than in culture medium. Round to globose, one to two celled conidia were also frequently observed.

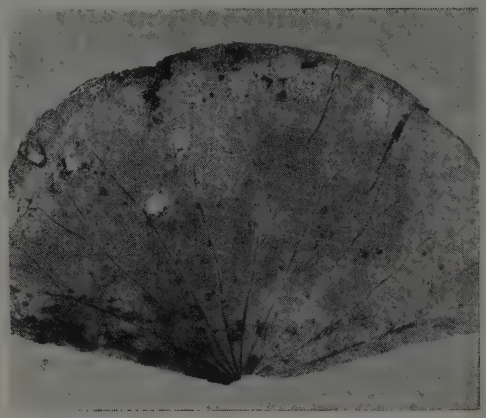

Fig 2.—A part of the infected leaf of *Nelumbium speciosum*.

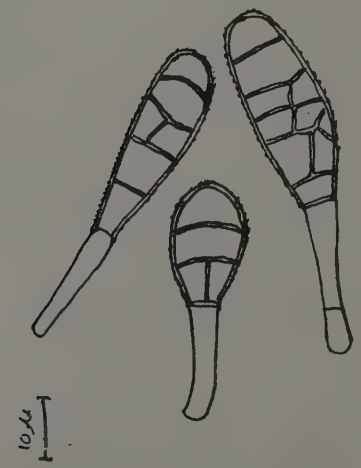

Fig. 1.—*Alternaria nelumbii* Enlows and Rand on *Nelumbium Speciosum*.

Locality: In a pond in the suburbs of Sukkur Barrage, Sukkur, Sind.

Date of collection: October 20, 1957.

Collected by: S.A. Qadir Junaidi.

Specimen: At the Mycological Herbarium of the Department of Botany, University of Karachi, and at the Commonwealth Mycological Institute, Kew, Surrey, England (Accession No. 71908).

Acknowledgement

The authors express their deep sense of gratitude to Dr. Ellis of Commonwealth Mycological Institute, England, for kindly checking the identification.

EFFECT OF LIGNIN ACETIC ACID IN THE ROT PROOFING OF COTTON YARNS AND JUTE FIBRES

RABIA KHANUM* AND Q. A. AHMED†

Department of Botany, University of Dacca, East Pakistan

The fungicidal properties of lignin acetic acid have previously[1] been studied against several fungi including *Memnoniella echinata*, and therefore in the present study an attempt has been made to find out whether lignin acetic acid could be used as rot proofing agent against fungal deterioration of cotton yarns and jute fibres. *Memnoniella echinata* and *Chaetomium globosum* were respectively selected as cellulolytic organisms for cotton yarns and jute fibres as they were found in the previous experiment[2] by the present authors to cause greater degradation of the strengths of yarns and fibres. The action of lignin acetic acid as a protectant was determined by growing the organisms on lignin acetic acid treated and untreated cotton yarns and jute fibres, and then testing their breaking strength.

Materials and Methods

In the earlier work on the use of lignin acetic acid as a fungicide,[1] a 1% solution had been found to check the growth for a period of 9 days, following which a slight growth was recorded. Therefore a slightly higher concentration, *viz.* 2% lignin acetic acid solution was used in the present study, and was prepared by dissolving 2 g. of the chemical in 5 ml. ethyl alcohol[1] and then mixing in 95 ml. water. The cotton threads and the jute fibres were placed on the microscope slides, tied at both ends[2] and then dipped in the above solution for 30 minutes. The excess solution was drained off and the material was allowed to dry. The slides with threads thus treated were placed in a raised condition on two pieces of glass rods within petri dishes containing 2 Whatman No. 4 filter papers. These were then autoclaved at 15 lbs. pressure for 15 minutes. To each dish 3 ml. sterilised water was added by means of sterilised pipettes. In the experiment both lignin acetic acid treated and untreated controls were kept along with the inoculated sets of treated and untreated sets for comparison. Inoculation was done by dusting the respective sets with spores of the organisms, *M. echinata* and *Ch. globosum*. All the sets were incubated at room temperature inside a glass chamber having theoretically 100% humidity.

Samples of cotton yarns and jute fibres were examined and tested for the breaking strength three times during the six weeks incubation period, i. e. every two weeks. Each time the yarns and fibres were removed from the petri dishes and carefully rinsed in 70 % ethanol to remove the fungal growth, after which they were washed in distilled water, the excess of water drained off and the fibre allowed to dry on filter paper. The air dried yarns and fibres were conditioned at 65% relative humidity for 24 hours before measuring the breaking strength of the fibres.

TABLE 1.—COMPARATIVE CELLULOLYTIC ACTIVITY OF *M. echinata* ON TREATED AND UNTREATED COTTON YARNS AT THREE INTERVALS OF TIME.

(L.A.A.=Lignin acetic acid)

Time elapsed	Mean breaking weight from ten measurements (in g.)			
	Control sets		Inoculated sets	
	Untreated yarns	L.A.A. treated yarns	Untreated yarns	L.A.A. treated yarns
Second week	279.3	276.0	100.4	129.0
Fourth „	273.2	267.8	80.7	94.7
Sixth „	264.3	261.1	48.7	79.4

*At present Lecturer in Botany, Dacca College, Dacca. †At present Plant Pathologist, Jute Research Institute, Dacca.

TABLE 2.—COMPARATIVE CELLULOLYTIC ACTIVITY OF *Ch. globosum* ON TREATED AND UNTREATED JUTE FIBRES AT THREE INTERVALS OF TIME.

Time elapsed	Mean breaking weight from ten measurements (in g.)			
	Control sets		Inoculated sets	
	Untreated fibres	L.A.A. treated fibres	Untreated fibres	L.A.A. treated fibres
Second week	41.2	40.9	22.0	35.5
Fourth „	40.1	39.4	12.5	29.5
Sixth „	39.0	37.1	6.5	19.1

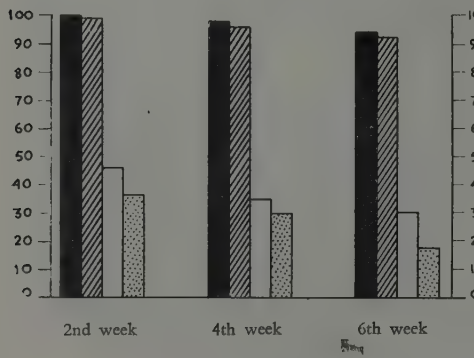

Fig. 1.—Percentage of strength of variously treated cotton yarns after three successive periods.

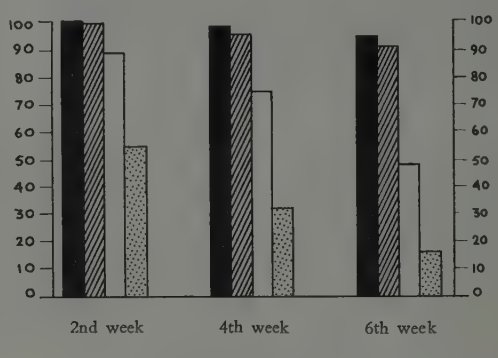

Fig. 2.—Percentage of variously treated jute fibres after three successive periods.

Control yarns.
Control yarns treated with L.A.A.
Memnoniella echinata on L.A.A. treated yarns.
M. echinata on untreated yarns.

Control fibres.
Control fibres with L.A.A.
Chaetomium globosum on L.A.A. treated fibres.
Ch. globosum on untreated fibres.

Results

After the second, fourth and sixth week of incu bation, the fibres were tested for their breaking strength, the individual fibre and yarn being clamped one by one to the measuring pan of the balance[2] and the breaking load determined. Table 1 shows the results obtained with cotton yarns against *M. echinata*. Results obtained with jute fibres against *Ch. globosum* are shown in Table 2.

Data presented in Table 1 showed that with cotton yarns treatment with lignin acetic acid solution as protectant did not prove suitable against the deteriorative activity of *M. echinata* (Fig. 1). The percentage of loss in the breaking strength of untreated yarns at 14, 28, and 42 days harvest periods was 63, 70 and 82 respectively. With lignin acetic acid treated cotton yarns the percentage of loss in breaking strength at the above three intervals of time was 53, 65 and 70 respectively, showing only an insignificant improvement over the untreated yarn.

With jute fibres, however, this treatment

yielded some positive result against *Ch. globosum* as would be noticed from Table 2 and Fig. 2. The percentage of loss in breaking strength of untreated fibres due to *Chaetomium* at 14, 28 and 42 days harvest periods was respectively 45, 69 and 84 while with lignin acetic acid treated fibres the percentage of loss in breaking strength at three such intervals of time was respectively 11, 26 and 52. It is probable that the use of lignin acetic acid in higher concentrations may prove even more effective.

Acknowledgment

The authors are indebted to Dr. M. H. Khundkar for supplying the lignin acetic acid.

References

1. M.I. Ali, Q.A. Ahmed & M.H. Khundkar, Pakistan J. Sci. Ind. Research, **1**, 79 (1958).
2. Rabia Khanum and Q. A. Ahmed, ibid., this issue.

INSECT AND FUNGUS PARASITES OF THE COMMON HOUSEFLY MUSCA DOMESTICA LINN.

M. S. Quraishi

Central Laboratories, Pakistan Council of Scientific and Industrial Resarch, Karachi

In the course of work on the breeding of houseflies for the insecticidal tests carried out at these laboratories it has been noted that they are attacked by three chalcidoid (order Hymenoptera) parasites and one fungus parasite.

Of the three chalcidoid parasites two have been identified as *Spalangia* sp. (family Pteromalidae)[1,2] and *Dirhinus* sp. (family Chalcididae).[3] The third awaits identification. *Spalangia* sp. has frequently been reported as parasitising housefly pupae in different countries of the world but, so far as the author knows, no species belonging to the genus *Dirhinus* appears to have been previously reported as a parasite of housefly pupae. Various *Dirhinus* spp. have, however, been noted as parasites of the genera *Ceratitis*, *Dacus*, *Glossina*, *Lucilia*, *Sarcophaga* and *Wohlfahrtia* etc.[1]

Life cycles of these parasites have now been studied in the laboratory. *Spalangia* sp. takes 20-25 days, *Dirhinus* sp. 25 to 30 days and the unidentified parasite 30-34 days for completion of the life cycle when the temperature varies between 78°F. to 90°F. and relative humidity between 69% to 79%.

Of these three *Spalangia* is the most active parasite. *Dirhinus* sp. will successfully parasitize and emerge out of almost all pupae if very young pupae (fresh to a few hours old) are parasitized. In case where older pupae are attacked by *Dirhinus* sp. the pupae develop to an advanced stage but the adult flies fail to emerge out and later on shrivel inside the pupal shell. The development of *Dirhinus* also seems to be greatly affected by temperature. When the minimum temperature falls below 76°F. *Dirhinus* takes about 60-70 days as against the normal of 25-30 days for the completion of its life cycle, and a number of parasites fail to emerge.

Houseflies in the laboratory have also been attacked by a fungus which has been identified as *Empusa muscae* (order: Entomophthorales),[4] Figs. 1 and 2. This fungus attacks the flies during the months of February and March in Karachi. The temperature in the laboratory varies, during these months, between 85°F. to 73°F. and humidity between 70% to 60%. DDT resistant strains of houseflies seem to be much more susceptible to the attack of the fungus than the non-resistant ones and in March, 1958, the DDT resistant strains of houseflies were thereby completely lost.

Fig. 1.—A housefly killed by *Empusa muscae*, showing the fungus spores on the wing and abdomen.

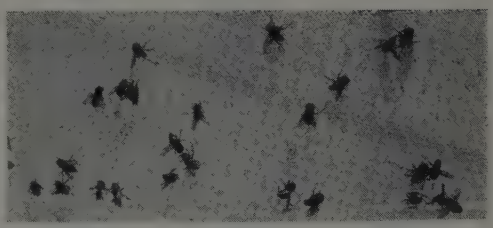

Fig. 2.—Houseflies killed by *Empusa muscae* sticking to the net wall.

References

1. W. R. Thomson, *A Catalogue of the Parasites and Predators of Insect Pests* (Imperial Agricultural Bureau Institute of Entomology, Parasite Service, Bellville, Ontario, Canada, 1943), Section 1, Part 2, p. 48.
2. A. D. Imms, *A General Textbook of Entomology*, (Methuen and Co. Ltd., London, 1942).
3. Hem Singh Pruthi and M. S. Mani, *Biological Notes on Indian Chalcidoidea, Misc. Bull No. 30*, (The Imperial Council of Agricultural Research, Manager of Publications, Delhi, 1940).
4. H. L. Sweetman, *The Biological Control of Insects* (Comstock Publishing Co., Inc., 1936).

A CLAVICORN BEETLE ASSOCIATED WITH LAC

S. Mahdihassan

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

Several years ago, the late Rao Bahadur C.S. Misra kindly made available to the author, a pound of fresh stick-lac, growing at Pusa, Bihar, on 'ber,' *Zizyphus jujuba*. The area, both geographically and ecologically, is similar to that of Rajshahi in East Pakistan, so that the present note may be of some interest for lac cultivation in the latter locality. The above-mentioned brood lac was received at Bangalore about the middle of Novemeber 1922. While dissecting individual lac cells, using a binocular microscope for immediate examination for anything requiring critical observation, the author came across pupae that appeared to be those of some unknown beetle. From this particular sample of lac some five pupae were collected, all after breaking the cells with a small sharp scalpel. The pupae were found externally to the bodies of lac insects but within their cells. No larva was found which could, otherwise, have been dissected to examine the stomach contents and ascertain the exact nature of the food and thus discover the relationship of the beetle to the lac insect. Its presence within the cell was however exactly the same, as for example, that of Silvanus Iyeri, a recognized beetle parasite of lac.[1]

Of the female pupae collected, one was laid on its back to expose its ventral appearance and Fig. 1 was drawn from it. Another was placed carefully sideways and its appearance is shown

Fig. 5.—Macrophotograph of the clavicorn pupae, the larger shows the ventral view of the female, the smaller two represent the male.

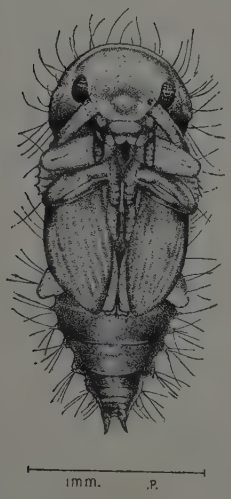

Fig. 1.—Female pupa of the clavicorn beetle, ventral view.

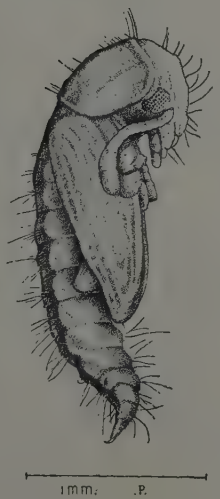

Fig. 2.—Same as Fig 1, side view.

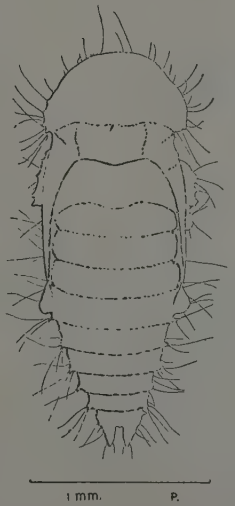

Fig. 3.—Same as Fig. 1, dorsal view.

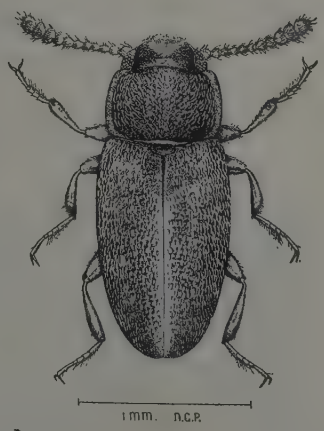

Fig. 4.—Female clavicorn beetle, adult, dorsal view.

in Fig. 2. These two pupae died, apparently due to outside atmospheric conditions, soon after the illustrations were made. Figure 3 shows a dorsal view of a third larva, which had to be left rather sketchy because of the short time for which the pupa could be exposed to the ambient condition if it was to survive till it could moult, which it did, and Fig. 4 was made from it. One female pupa, seen ventrally, and two pupae of the male insect were photographed on an enlarged scale as shown in Fig. 5. Excepting one female (Fig. 3) no other pupa survived to become adult.

Before the last World War, a specimen of this particular beetle was sent to a Coleoptera specialist, who could not, however, identify it with any known species. The specimen had become slightly mouldy, but none better could be obtained so far. This beetle was not observed again by the author in any lac, but it is hoped that workers in the Rajshahi region will have an apportunity of doing so.

Reference

1. Silvanus Iyeri, Current Sci. (India), **24**, 418 (1955).

NON-TECHNICAL NOTES

DENATURANT FOR METHYLATED SPIRIT

The present annual requirement of methylated spirits may be assumed to be approximately 200,000 gallons, but it will probably increase along with the general development of the country's technology. Even this present requirement is not being met because of the lack of availability of denaturants. Generally, as prescribed by the Provincial Governments, caoutchoucine and pyridine are used as denaturants to the extent of 0.5% each. As there is no industry in Pakistan which can supply these materials, they have to be imported from abroad at a very high cost, nearly Rs. 50 per gallon for either of them. Since a total of 1% denaturant is used the cost of denaturing one gallon of spirit is 8 annas. Besides the high cost these materials are in short supply in other countries, and difficulty is therefore experienced in obtaining enough for our use. As a result of work carried out in the Central Laboratories of the Pakistan Council of Scientific and Industrial Research, a process has been developed to give high yields of caoutchoucine from waste rubber. The process essentially consists in subjecting the waste rubber to distillation in a current of super-heated steam in the presence of a catalyst, and fractionating the distillate and sulphurating it.

The capital investment in a unit of production with an annual capacity of 3000 gallons of denaturant is estimated at Rs. 42,000 with an average cost of Rs. 19/8 per gallon of denaturant as against about Rs. 50 for imported material.

Equipment and Raw Materials

The equipment would consist of the following: disintegrator, boiler with super heater, distillation tower, and refluxing equipment.

The raw materials required in the process are: waste rubber, chemicals, and sulphur.

Pre-Construction Cost Estimation

(Production capacity = 10 gal. per day on 3000 gal. per annum).

	Rs.	Rs.
Capital expenditure		
Equipment	15,000	
Building	13,000	
		28,000
Running expenditure (per annum)		
Raw materials ..	37,680	
Direct wages ..	5,400	
Containers	3,000	
Power	1,500	
Contingencies ..	2,000	
Depreciation @ 4% ..	2,800	
		52,380
Indirect expenses		
Promotion of the project @ 2 1/2% on Rs. 42,000 (= Capital investment)		1,050
Selling expenses		1,800
Interest on capital @ 4% on Rs. 42,000.		1,680
Insurance @ 2 1/2 % on Rs. 65,000.		1,642
Cost of production of 3000 gallons of denaturants		58552

Average cost per gallon: Rs. 19/8.

INSULATING TAPES

A dielectric or insulating material may be characterised roughly as having an electric conductivity of less than 10^{-6} mhos/cm. Materials with conductivities in the range of 10^{-6}–10^{-3} mohs/cm. are semi-conductors. Usually, mechanical, chemical, thermal and cost considerations determine the choice of an insulating material. The cheapest and the simplest form of insulation is the insulating tape made of cloth or paper and coated with an insulating material. Even this type of insulating material is imported in Pakistan. It is estimated that Pakistan consumes annually about 3 lakh spools of 1/2" width and 50 yards length. A spool of these measurements imported from abroad costs about Rs. 2 to Rs. 2/8.

As a result of investigations carried out at the Central Laboratories of the Council of Scientific and Industrial Research, Karachi, it has been possible to evolve a process for the manufacture of insulating tape from exclusively indigenous raw materials. The tape is about 100% above the British Standards Specifications (B.S.S.).

The total capital investment for a unit of production for manufacturig 300,000 spools (1/2″×50 yards) per annum is estimated at approximately Rs. 2,14,000. The average cost of a spool in a unit of this size works out to Rs. 1/7, inclusive of overhead expenses, as against the present market price of Rs. 2 to Rs. 2/8.

Process, Equipment and Raw Materials

The process involves the following unit operations: mixing the various ingredients, coating of the tape, drying of the tape at controlled temperature and winding of the tape and cutting into spools of required sizes.

The equipment required for the process consists of : jacketted vessel with mixing and temperature control device, bath for coating purpose, drying chambers and winding and cutting machine.

The raw materials required are: insulating medium, vehicle, filler and cloth.

All these materials are available in the country.

Pre-Construction Cost Estimation

(Production capacity =3 lakh spools per annum)

Capital expenditure

	Rs.	Rs.
Equipment	70,000	
Building	43,000	
		1,13,000

Running expenditure (for 3 months)

Raw materials ..	85,275	
Direct labour ..	3,330	
Indirect labour ..	3,210	
Selling expenses ..	1,260	
Packages, power, interest on capital and contingencies	7,865	
		1,00,940
Total capital investment		2,13,940
Cost of production of 3 lakh spools		4,28,763

Average cost Rs. 1/7 per spool.

HEAT AND SOUND INSULATION BOARDS FROM SUGAR-CANE BAGASSE AND OTHER AGRICULTURAL WASTES

Sugar-cane bagasse, reeds, coconut fibre, rice husks and similar other materials find little economic use and are wasted in considerable quantities. For instance, bagasse which is a by-product in the process of cane crushing is mainly used as a cheap fuel for boilers in sugar-cane factories, but even after meeting the requirements of fuel, large quantities are left over as surplus for which there is practically no use.

With a view to utilise these materials, investigations were undertaken in the Laboratories of the Council of Scientific and Industrial Research, and it has been possible to evolve a commercially feasible process for the manufacture of low-cost heat and sound insulation boards which can be used in buildings for partitions, false ceilings, etc. These boards have a thermal conductivity of 0.09 (same as glass wool), 1 inch thickness of the board being roughly equivalent to 10 inches of brickwork in respect of insulation, and a tensile strength of 90 lbs. per sq. inch. These boards can also be used for light weight roofs in a sandwich system of water proof material. On account of the light weight of the roof, made of sandwiched boards, the supporting structure and the load-bearing walls need not be as strong as would be necessary for any other normal type of roof, thus resulting in a considerable amount of saving in the overall construction cost.

The total capital investment for a unit producing annually 60,000 boards of 8″×4″×1″ thick is estimated at approximately Rs. 5,25,000. The average cost per sq. ft. of the board in a unit of this size is estimated at 2¼ annas. The market price of similar board is 8 to 10 annas per sq. ft.

Process, Equipment and Materials

The process of manufacturing these boards consists of the following unit operations : shredding, cooking, mixing and beating, pressing in moulds, and drying.

The process is simple, requiring very little specialised knowledge or technical know-how,

and can be carried out by semi-skilled labour with limited overall technological supervision.

The basic equipment required consists of: shredder, pressure cooker, beater, hydraulic press, and drying chamber.

With the exception of the last item which can be constructed locally, the other items of the equipment will have to be imported.

The raw materials required in the process are: bagasse, reeds, coconut fibre, and chemicals.

All these materials are easily available in the country.

Pre-Construction Cost Estimation

(Production capacity = 60,000 boards of 8″×4″×1″ per year).

Capital expenditure	Rs.	Rs.
Equipment		3,50,000
Running expenditure (per annum)		
DIRECT EXPENSES		
Raw materials ..	1,01,000	
Direct wages ..	48,000	
Power	15,000	
Contingencies ..	6,000	
Depreciation @ 10% ..	45,700	
		2,15,700
INDIRECT EXPENSES		
Establishment ..	18,360	
Promotion of the project @ 2 1/2% on 5 1/4 lahks (= capital investment)	13,125	
		31,485
Selling expenses		12,600
Interest on capital @ 4% on Rs. 5 1/4 lahks.		21,000
Insurance @ 2 1/2% on Rs. 5,58,000.		13,950
Total cost of production for 60,000 boards		2,94,735

Cost per board = Rs. 4/14/7, say Rs. 5

Cost per sq. ft. = Rs. 0/2/6

FOUNTAIN PEN INKS

The making of writing ink is a very ancient art. The earliest inks consisted of lamp black ground with glue and moulded into sticks which were mixed with water before use. Such inks were used in the early Egyptian and Chinese civilizations as early as 2500 B. C. There are references to iron-gallo ink solutions of an iron salt, usually ferrous sulphate, in extracts of tannin bearing materials dating back to 210 B.C. Prior to the modern era of wide spread manufacture and distribution of goods, the making of writing ink was a household art. The present day writing ink industry, although very old, is relatively small and highly competitive, and the exact composition of the product is the individual manufacturer's secret.

The present annual consumption of fountain pen ink, in Pakistan, which has an upward trend is estimated at 30,000 gal., valued at about Rs. 1,000,000, of which about 50% is imported.

The locally produced inks are, however, of a very poor quality, necessitating the continued import of high quality inks from abroad. The ink produced according to the process developed in the Council's laboratories has been found, to be comparable with the best imported brands.

The total capital investment for a production unit with a capacity of 7000 gallons per year is estimated at Rs. 100,000, and the average cost of one fluid oz. bottle of ink would be 3 annas as against one rupee for a similar quality of imported ink.

Process, Equipment and Raw Materials

The unit processes involved are: preparation of distilled water, preparation of the various solutions, mixing of the solutions, ageing of the ink, centrifuging, filling the bottles, capping the bottles, labelling, and packing.

The equipment required consists of: water distillation plant, agitators, mixers, filters, centrifugal separating machine, mixing tank, air tight storage tanks, filling machine, bottle capping machine, bottle washing machine, labelling machine, and packing machine.

The last four machines are not very essential and can be dispensed with.

The raw-materials required are: dyes, acids, and some chemicals.

Pre-Construction Cost Estimation

(Production capacity = 7000 gallons per year)

Capital expenditure

	Rs.	Rs.
Equipment	28,000	
Building	26,600	
		54,600

Running expenditure (for 6 months)

Raw materials ..	13,800
Direct labour ..	4,980
Establishment ..	6,240

	Rs.	Rs.
Selling expenses	2,400	
Packages, power, interest on capital and contingencies	15,000	
		42,420
Total capital investment		97,020
Say:		100,000

Cost of production of 7000 gals. of ink per year: Rs. 89,855

Average cost of ink: Rs. 13 per gallon.

PATENT NEWS

Abridgements of patent specifications of Pakistani inventors notified as accepted during December 6, 1957 to October 3, 1958 in the Part IV of the Gazette of Pakistan

107598 *Chilam for hubble-bubbles and like smoking appliances.* A.H. KHAN, K. U. KHAN, G. U. KHAN AND M. U. KHAN.—The chilam is provided with an electrically heated coil. A porcelain plate is placed in between the heating coil and the tobacco, above which a disc of earthen ware or stone is placed.

107608 *Keyboard of typewriting machine in Bengali script.* A. A. KHAN.—The keyboard comprises letter-matrices and type-bodies of characters of Bengali for type-writing, teleprinting, monotyping and lino-typing purposes.

107691 *A hand operated injection moulding machine for the manufacture of plastic articles.* HAJI A. A. ZIA.—The machine comprises a vice assembly, die, injection chamber, means for heating the injection chamber, means for forcing the plastic material into the die and means for feeding the plastic material into the injection chamber.

107709 *A process for preserving milk, neera and like perishable liquids.* M. A. KAZMI.—Milk, neera and like perishable liquids are preserved by filling a bottle or like container with the liquid, heating it to a predetermined temperature, closing or sealing it air-tight at that temperature and allowing the bottle or container to cool under air-tight conditions, leaving above the liquid a natural vacuum formed by the contraction of the heat-expanded liquid.

107742 *A mechanical tube well bucket.* S. M. ISMAIL.—The bucket comprises three piston rings, an operating valve, a bucket to raise water from a tube well, a pin, two tube spacers of thin metal round the pin for maintaining in a central position a connecting rod which is attached to the handle of a pump used by hand or by machine. The piston rings operate in the grooves ordinarily to be found in a piston head, as a piston of an ordinary internal combustion engine but in an inverted position.

107743 *A hand driven paddy dehusking machine.* S. M. ISMAIL.—The machine has a receptacle wherefrom paddy is led to a helix and thereon to rotor knives mounted on the main shaft. The friction resulting from rotor knives, an adjustable stripping knife and a perforated semicircular sieve dehusks paddy which falls out.

107744 *Double locking padlocks.* S. M. ISMAIL.—The device relates to a padlock, wherein two ends of a U-shaped hasp or shackle are adapted to be unlocked in succession within the padlock casing, having the locking mechan

ism in it by the continued turning movement of one and the same key in any direction.

107859 *A process for the simultaneous production of refined shark liver oil and vitamin A concentrates alongwith the recovery of other therapeutically active by-products.* S. MAHDIHASSAN, M. MOINUDDIN, S. MAQSOOD ALI AND S. ABDUL HAQ.—This journal, **1**, 250 (1958).

107883 *A frame for the protection of paper on bail roll rod of typewriting machine.* ABDUL WAJID. A rectangular-shaped frame, made of wire, is fitted into a side lock placed at each end of the bail roll rod of a typwriter. The device prevents paper from flying into the typewriting machine.

107923 *A type fount for manual and mechanical composing in naskh script.* A. A. KHAN.—In typefounts and typebodies for printing in naskh script adapted to be used essentially for printing in Arabic, Persian and Urdu, the characters are cast on the bodies complete with dots or other diacritical marks.

108018 *A process for the continuous refining of sulphur ore.* IQBAL AHMED AND KARIMULLAH.—This Journal, **1**, 250 (1958).

108139 *Gas plant using cattle dung as fuel.* TAJ JILANI.—The plant for producing combustible gas from cattle dung consists of two mild steel drums, one above the other in a telescopic arrangement, and two pipes serving as means to supply the gas to the burner from the top drum.

NOTES & NEWS

Making Magnetic Fields Visible

An interesting method has been devised for making magnetic fields visible wherein the picture is formed by the light reflected from the faces of thin plate-like crystals of α-Fe_2O_3 in an aqueous suspension. The crystals have a high magnetic anisotropy and therefore they are oriented even by a very weak magnetic field without any appreciable translational motion. [J. App. Phy., **29**, 223 (1958)].

AGR Project

Sir John Cockcroft in his James Forrest lecture released details of the Advanced Gas-Cooled Reactor (A G R) project, which the U.K. Atomic Energy Authority has been studying for some time, with the objective of reducing overall dimensions and capital cost of reactors by nearly 30% through an increase in the surface temperature of the fuel elements to about 600°C. Ceramic fuel elements, probably beryllium clad, will be used in the reactor since experiments have shown that such elements have suffered no damage when thermo-cycled several hundred times through the alpha-beta phase change. The design changes will of course decrease the neutron economy and some enrichment will be necessary, possibly in the neighbourhood of a 30% increase in U^{235} content over natural uranium. [Nuclear Eng., **3**, 140 (1958)].

German Honour for Dr. Salimuzzaman Siddiqui

The Diploma of Doctorate of Medicine honoris causa conferred upon Dr. Salimuzzaman Siddiqui by the Faculty of Medicine of the Johann Wolfgang Goethe University of Frankfurt on Main, was presented to him at a ceremony at the West German Ambassador's residence in Karachi on the 22nd October 1958.

The citation read out by the West German Ambassador, Herr H. C. Podeyn, in the presence of a distinguished gathering, said :

"The medical faculty confers this distinction on a scholar who in his country has promoted chemical research and teaching in an excellent way, who has contributed fundamentally to the investigation of alkaloids from rauwolfia and other tropical plants, and who has thus enriched medicine with valuable drugs."

The Ambassador also announced that the German Pharmaceutical Society of Tubingen had decided to elect Dr. Siddiqui corresponding member of the Society, adding that this was an international recognition for scientific work carried out in Pakistan.

Applications Filed in the Patent Office

The number of applications for patents filed in the Pakistan Patent Office during the years 1951-1957 by persons residing in various countries is given below. The period covered under each column is from April to March.

Country	1951-52	1952-53	1953-54	1954-55	1955-56	1956-57
Pakistan ..	23	25	32	32	28	38
U. K. ..	314	314	297	299	287	247
Switzerland ..	67	65	133	171	151	162
U. S. A. ..	89	87	115	136	127	121
Germany ..	56	60	61	72	72	82
France ..	55	39	36	41	44	70
Netherlands	13	34	24	28	37	44
Italy ..	17	33	33	14	27	30
Sweden ..	18	14	9	16	14	19
India ..	17	13	6	15	8	7
Australia ..	9	7	5	12	11	6
Denmark ..	9	12	12	8	2	6
Belgium ..	7	7	6	7	7	10
Union of South Africa	9	6	4	4	8	12
Japan ..	1	4	2	9	9	12
Canada ..	3	5	8	10	9	1
Norway ..	—	5	5	9	5	3
Liechtenstein	—	2	9	7	4	4
Spain ..	4	1	4	6	5	5
Austria ..	5	3	—	10	1	2
Hungary ..	2	1	4	2	2	5
Ireland ..	—	2	1	—	1	9
Czechoslovakia	—	—	—	3	6	3
Morocco ..	—	1	1	6	4	—
Tangier ..	—	2	3	—	2	1
Panama ..	—	2	4	—	1	1
Finland ..	1	1	—	—	2	3
Argentina ..	—	—	3	1	1	—
Philippines ..	—	—	4	—	1	—
Luxembourg	—	—	—	—	1	1
Indonesia ..	—	1	—	—	1	—
Yugoslavia ..	—	—	—	1	1	—
Southern Rhodesia	—	—	—	—	1	—

Awards for Inventors and Scientists

The Government of Pakistan have decided to give awards to deserving Pakistani scientists and inventors of new and useful processes, patents for which have either been taken out or have been applied for. This is to provide the inventor in Pakistan with: (i) opportunities for experimentation, development and perfection of inventions and (ii) interest in the exploitation of patents. A committee consisting of eminent scientists and educationists in the country has been set up by the Government to examine claims for awards and judicious utilisation of the fund.

Forthcoming International Conferences

135th Meeting of American Chemical Society; April 5-10, 1959; Boston, Mass., U.S.A.

International Conference on Co-ordination Chemistry; The Chemical Society; April 6-11, 1959; London.

5th World Petroleum Congress, (Permanent Council of the World); May 30 to June 6, 1959; New York, U.S.A.

International Plastics Exhibition and Convention (Formerly the British Plastics Exhibition and Convention); June 17-27, 1959; Olympia, London.

XVth International Dairy Congress; June 29 to July 4, 1959; London.

Fifth International Congress on Glass; June 29 to July 4, 1959; Munich, Germany.

Canadian Medical Association, 92nd Annual Meeting in conjunction with British Medical Association; July 16-24, 1959; Edinburgh, Scotland.

21st International Congress of Physiological Sciences; August 9-15, 1959; Buenos Aires, Argentine.

10th International Congress of International Institute of Refrigeration; August 19-26, 1959; Copenhagen, Denmark.

9th International Botanical Congress. International Union of Biological Sciences (IUBS); August 19-29, 1959; Montreal, Canada.

2nd World Conference on Medical Education (World Medical Association); August 30 to September 4, 1959; Chicago, Illinois, U.S.A.

9th International Congress for the History of Science; August 30 to September 6, 1959; Barcelona and Madrid, Spain.

17th International Congress of Pure and Applied Chemistry and 20th Conference of the International Union of Pure and Applied Chemistry (IUPAC); August 30 to September 6, 1959; Munich, Germany.

136th Meeting of American Chemical Society; September 13-18, 1959; Atlantic City, New Jersey, U.S.A.

American Association for the Advancement of Science; Annual Meeting; December 26-31, 1959; Denver, Colorado, or: Cleveland, Ohio, U.S.A.

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